A METHOD FOR THE PREVENTION OF N_2O_4 FLOW DECAY

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Boeing Company

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The Boeing Company
Aerospace Group
Seattle, Washington 98124

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Air Force Rocket Propulsion Laboratory
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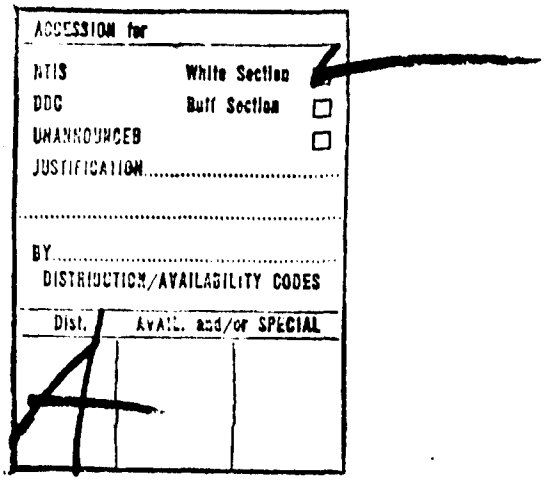

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13. ABSTRACT

This document discusses the results of a program whose objective was to formulate a method for preventing the occurrence of N_2O_4 flow decay. The method, which was successfully demonstrated, consisted of the removal of the flow decay causing contaminants (nitrate complexes of iron) from the N_2O_4 by distillation or filtration. The resulting iron-free N_2O_4 could be stored in contact with various alloys (even a ferrous alloy, such as 347 stainless steel) for substantial periods with no significant recontamination occurring.

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A METHOD FOR THE PREVENTION OF N_2O_4 FLOW DECAY

FINAL REPORT

K. E. PULLEN, T. L. SMITH, J. P. STEBBINS

I-C

FOREWORD

The work in this program was performed at The Boeing Company, Seattle, Washington, for the Air Force Rocket Propulsion Laboratory under Contract No. F04611-72-C-0040, Project No. 3058, BPSN: 623058, during the period from January 1 through September 30, 1972. The program was administered under the direction of Capt. Charles Mastromonico of the Rocket Propulsion Laboratory, Edwards, California.

The project was managed at The Boeing Company by Mr. James R. O'Brien of the Aero/Propulsion Department. Dr. Kent Pullen and Mr. T. Lynn Smith were responsible for the technical execution of the program with the cognizance of Mr. James P. Stebbins, Principal Investigator.

This technical report has been reviewed and is approved.

Charles R. Mastromonico
Captain USAF
Project Engineer

TABLE OF CONTENTS

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES
(Continued)

LIST OF TABLES

1.0 SUMMARY

A number of basic investigations conducted under governmental and industrial funding have outlined the role played by iron-containing compounds in causing flow decay. However, until the present study a positive method for its elimination or control was undefined. The objective of this program was to define a practicable technique to eliminate flow decay as a problem from operational weapon and space systems. Three tasks were performed in achieving this goal: (1) Removal of iron from specification grade N_2O_4, (2) Determination of the rate of iron contamination of N_2O_4 in contact with various metal alloys, and (3) Execution of flow tests in which N_2O_4 was passed through a simple, filtered system under conditions conducive to flow decay.

Distillation and filtration were shown by radioisotope tracer techniques to be methods of removing iron from brown N_2O_4. Radioactive iron-59 was added to samples of N_2O_4 which were then distilled or filtered. Following these operations the N_2O_4 was checked in a multichannel analyzer for the presence of radioactivity. Within the measurement limits of the instrumentation, distillation appeared nearly 100% effective in removing iron. Filtration through sintered glass filters and through screen-type stainless steel filters was of limited effectiveness and pointed to adsorption as the primary filtering mechanism. A column packed with molecular sieve material was shown to be a very effective filtering agent.

The rates of dissolution of iron from 2014 aluminum, 6Al-4V titanium, and 347 stainless steel by N_2O_4 were measured by immersing radioactive samples of the alloy in N_2O_4. After immersion the alloy samples were removed and the solutions were examined for radioactivity. No iron was detected in the N_2O_4 containing the titanium or aluminum samples. However, radioactivity from some unidentified element was found in the N_2O_4 containing the titanium sample, which indicates a reaction with the sample had occurred. The reaction rate of N_2O_4 with 347 stainless steel varied directly but not linearly with the sample surface to propellant volume ratio.

Iron-free N_2O_4, prepared by distillation, was stored for approximately two months in tanks made from the three sample alloys. Following storage the N_2O_4 was flowed through a 2 micron stainless steel filter under conditions known to be conducive to flow decay. No decay was found with the N_2O_4 stored in the 2014 aluminum or 347 stainless steel tanks. About 15% decay occurred with that stored in the 6Al-4V titanium tank. The cause of this decay has not been clearly identified.

Flow decay resulting from passage of N_2O_4 through 2 micron nominal, stainless steel filters was studied as a function of N_2O_4 iron concentration. With new filters no flow decay occurred when less than 3.6 PPM iron (as iron nitrate) was added to the as-received N_2O_4.

Following successful laboratory experiments with molecular sieves, a larger molecular sieve filter, suitable for field use, was constructed for purifying N_2O_4. Approximately 200 lbs of as-received N_2O_4 (containing ~0.5 PPM iron) was filtered through 2 lb of Linde, type 13X, molecular sieves of 100/120 mesh. During the filtration a sample of that filtrate was withdrawn following each 18 lb increment of flow. These were examined by atomic absorption spectroscopy for iron concentration. No iron was detected in any of the samples since the readings did not exceed the instrumental detection threshold. The propellant to filter mass ratio was 1000 and the filtered propellant remained well within the specification limits. Filtration through molecular sieves thus appeared to be a practicable technique to eliminate flow decay as a problem from operational weapon and space systems.

2.0 INTRODUCTION

The phenomenon of flow decay has been experienced, identified and studied for the past seven years. A number of basic investigations have been conducted under government and industry funding. Foremost among these are Rocketdyne's studies for the Air Force Rocket Propulsion Laboratory (AFRPL) (e.g., References 1-3) and TRW's work for the National Aeronautics and Space Administration (e.g., References 4, 5). Valuable insights were gained in these studies, which elucidated the physicochemical nature of the phenomenon. None of them, however, have resulted in the development of a workable engineering solution to the problem, i.e., a procedure whereby propulsion systems of critical interest (such as the Titan Transtage and the Minuteman III Post Boost Propulsion System) may be rendered free of mission failures brought about by the occurrences of flow decay.

During N_2O_4 flow decay studies at the Boeing Company[6,7] which employed very sensitive radioactive tracer techniques it was observed that the clogging iron complexes which occurred in green N_2O_4 (MSC-PPD-2A) could apparently be removed by distillation. Radioisotope counting experiments further suggested that filtration efficiencies of various filters used to remove the iron complexes could be effectively and accurately measured with tracer methods. Since distillation and filtration are common engineering purification techniques it was natural to think in terms of iron complex removal as a solution to the flow decay problems of operational rocket systems. As a consequence, a contact was made with the Air Force Rocket Propulsion Laboratory and a program was evolved whose objective was to define a practicable method to prevent the occurrence of flow decay within systems utilizing brown N_2O_4.

3.0 TECHNICAL PROGRAM DEFINITION

The program consisted of three principal tasks using specification grade (MIL-P-26539C, Composition NTO), nitrogen tetroxide: (1) the removal of iron contaminants from N_2O_4 to a level below which flow decay did not occur, (2) the determination of the contamination rate of N_2O_4 in contact with typical aerospace tankage materials, and (3) the study of flow decay experienced by N_2O_4 flowing through filters.

3.1 Task 1 - The Removal of Iron From N_2O_4

Iron contaminants were removed by distillation and filtration. Distillations were performed at atmospheric and reduced pressures. Filtrations were performed for various types and sizes of filters and at different temperatures.

3.2 Task 2 - Contamination of N_2O_4 by Dissolution of Tank Metals

The rate of buildup of iron contaminants in distilled N_2O_4 was determined as a function of tankage material, surface-to-volume ratio, temperature and degree of agitation. The tankage alloys investigated were 347 stainless steel, 2014 aluminum, and 6Al-4V titanium.

3.3 Task 3 - N_2O_4 Flow Decay in Screen Filters

Nitrogen tetroxide was passed through filtering systems (typical of those used during propellant transfer) at conditions highly conducive to flow decay. Tests were run at increasing iron concentration until pronounced flow decay was observed. The iron-contaminated N_2O_4 was then purified by passage through an operational-type molecular sieve filter, which resulted in the elimination of flow decay during subsequent flow tests.

An additional set of flow tests were conducted with initially iron-free N_2O_4 stored in tanks made of the construction materials tested in Task 2.

4.0 REMOVAL OF IRON FROM N_2O_4

The general technique for studying iron removal was to add definite miniscule amounts of radioactive iron-59 to known weights of N_2O_4 and then to measure changes in radioactivity level resulting from distillation or filtration operations. Specifically a one c.c. liquid radioactive source of iron nitrate dissolved in concentrated nitric acid was prepared whose initial activity was one millicurie. Stock solutions of radioactive brown N_2O_4 were prepared by adding 10 microliters of the primary source liquid to a flask containing 155 grams of N_2O_4. The quantities of iron (about 2 ppb) and water equivalent (0.0065%) thus added were not large enough to perturb the concentrations of iron and water actually present in the N_2O_4.

Counting (iron-59 detection and measurement) was accomplished with the aid of a 3" x 3" sodium iodide detector having a 1.2" x 2.4" well (Harshaw Company). The multiple phototube output was amplified by a charge sensitive preamplifier (designed by Boeing) followed by a Technical Measurement Corporation Model CN1024 multi-channel analyzer. A simple Geiger counter was found to be sufficiently sensitive to allow a rapid semi-quantitative mapping of the iron distribution in both the distillation and filtration apparatuses.

4.1 Distillation

The distillation tests were performed with 5 c.c. samples of N_2O_4 in pyrex containers shown typically in Figure 1.

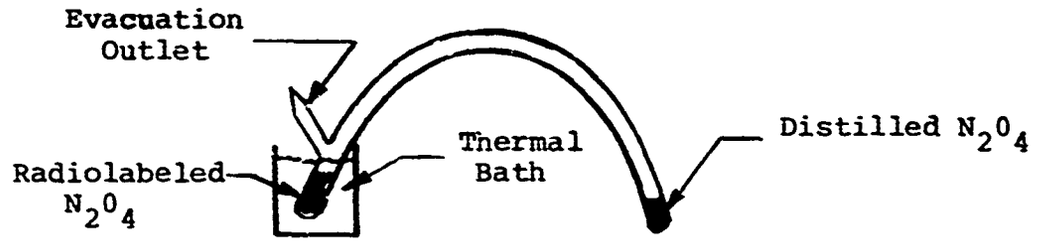


FIGURE 1 - DISTILLATION SYSTEM SCHEMATIC

4.1.1 Procedure

The container was manufactured, cleaned, evacuated (to effectively remove water adhering to the inside walls) and filled with gaseous dry nitrogen at 14 atmospheres. Cooled radiolabeled N_2O_4 was admitted to one leg of the tube and then carefully frozen with liquid nitrogen. The residual nitrogen was then pumped out, the evacuation outlet closed by fusion, and the N_2O_4 allowed to come to ambient temperatures. The empty leg of the tube was then immersed in liquid nitrogen, which condensed the N_2O_4 vapors. The low vapor pressure which resulted from the low temperature leg permitted a complete transfer of the liquid to the cold side in 25 minutes. A beaker filled with water at room temperature served as a thermal bath.

A second run was made with another tube to determine the feasibility of liquid transfer at a vapor pressure of about 1 atm. Temperatures were selected at values typical of those that could be encountered in a solar distillation. In this case the radiolabeled solution was immersed in a large thermos of water at a temperature of 37°C, the cold side being maintained at room temperature (22°C). This transfer required an hour and a half.

The bottom of the dry leg of the distillation tube was heated to 66° ± 2°C, a relatively high distillation temperature, for 30 minutes to see if $Fe^{59}(NO_3)_3$ would volatilize under these conditions. No volatilization of the radioactive residue was observed

4.1.2 Results

No carry over of radioactivity was detected within the statistical uncertainty of the counting experiments, ± 2 1/2% at 90% confidence level. Distillation was thus seen to be a technically feasible method for removing iron contaminants from N_2O_4.

4.2 Filtration

The first tests were performed with 10mm diameter sintered glass filters using 10gm portions of N_2O_4. The small quantities of N_2O_4 were chosen for convenience; the sintered glass filters were used as part of an all-glass system to avoid any possible interference from extraneous iron. The radioactive iron content of the N_2O_4 which was removed by the filter was measured and compared with the original activity to determine filtration efficiency. Two porosities of filters, 4 to 5.5 microns and 40-60 microns, were used at each of three different filtration temperatures. Larger quantities of N_2O_4 were then filtered to define the role of adsorption in the filtering mechanism. Other filters which were investigated included a 2 micron nominal, 10 micron absolute stainless steel filter (Western Filter Company, part number S12-19310-2), glass wool, and Linde Co. type 13X molecular sieves. The 10 micron absolute stainless steel filter was chosen because of its previous use in flow decay studies.[4,7] Glass filter frits having comparable pore sizes were selected to identify possible surface material effects. Glass wool and molecular sieves were chosen for study as adsorption filters due to their large surface to mass ratios.

4.2.1 Procedure for Testing Sintered Glass Filters

The apparatus used for the investigation of glass filters is shown in Figures 2 and 3. The beaker surrounding the tube containing the filter was made liquid tight at its junction with the filter tube with a putty sealant and was then filled with liquid at the appropriate filtration temperature. Radio-labeled N_2O_4 contained in the upper flask was brought to thermal equilibrium by passing it very slowly over the walls of the tube and through the filter. The lower graduate was used to catch the filtrate and contain it during counting. The filter tube was also removed and the sintered glass frit counted. The filter efficiency was determined as the ratio of the counts of the frit to the sum of the counts from both the frit and the filtrate.

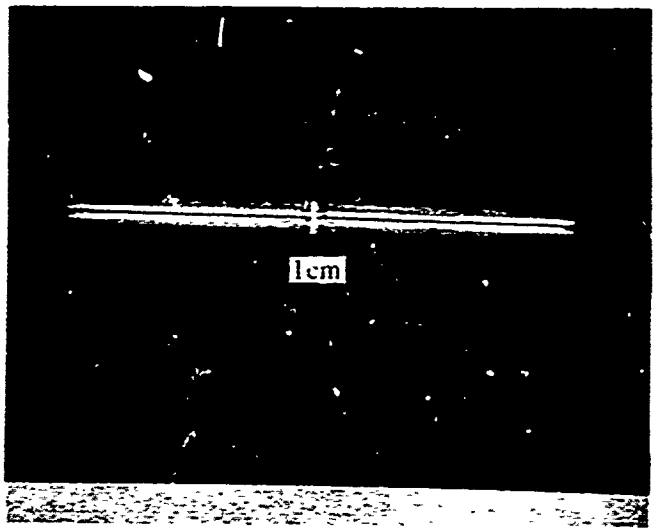


FIGURE 2. TYPICAL GLASS FILTER

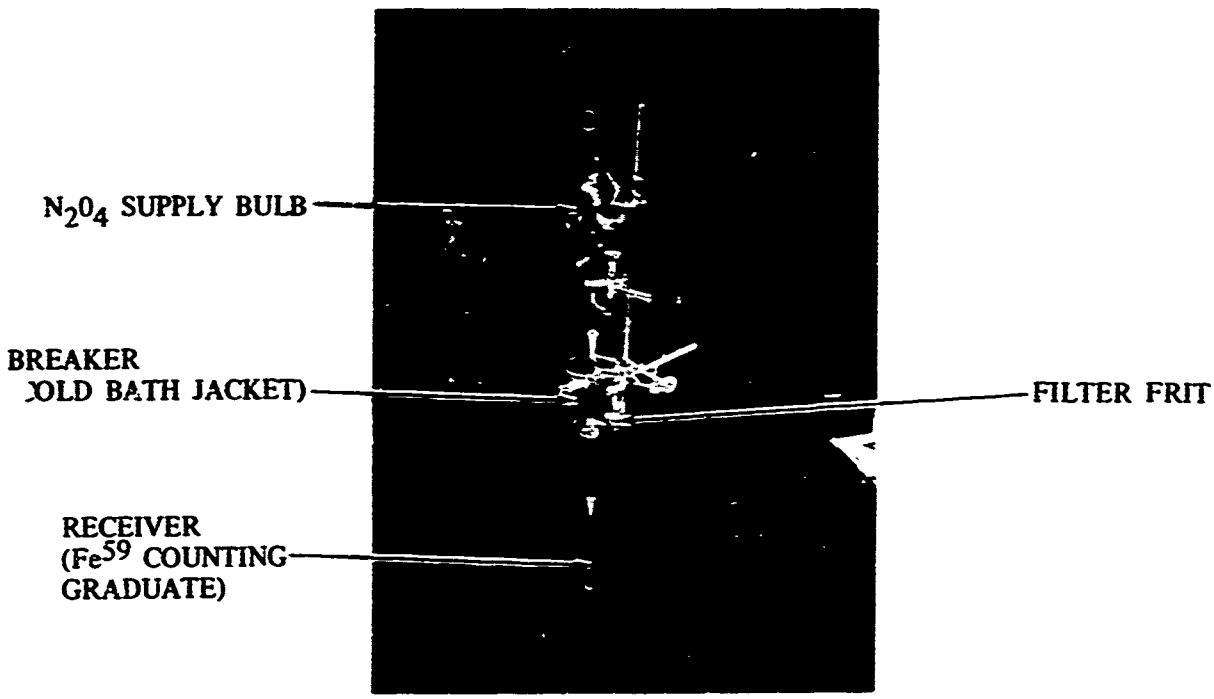


FIGURE 3. GLASS FILTER SYSTEM

Filtration thru coarse (40-60 micron, Van Waters and Rogers, catalog number 32592-023) and fine (4-5.5 microns, catalog number 32584-029) filters, was accomplished at room temperature, 0°C, and -10°C. The 0°C temperature was achieved with an ice bath and the -10°C temperature was obtained by cooling an aqueous solution of KCl with liquid nitrogen until a slush was formed.

The contribution of adsorption to the filtering process was investigated by filtering incremental amounts of a radiolabeled solution of P_2O_4 through a fine frit at room temperature. The activity of successive 10 gm portions of filtrate were measured to see if there was an increase in activity, which would correspond to the saturation of adsorption sites.

4.2.2 Results of Filtration Through Glass Frits

Although complete removal of iron by filtration was not accomplished substantial reductions were obtained as shown in Table 1.

Table 1 - Filtration Efficiencies of Glass Frits

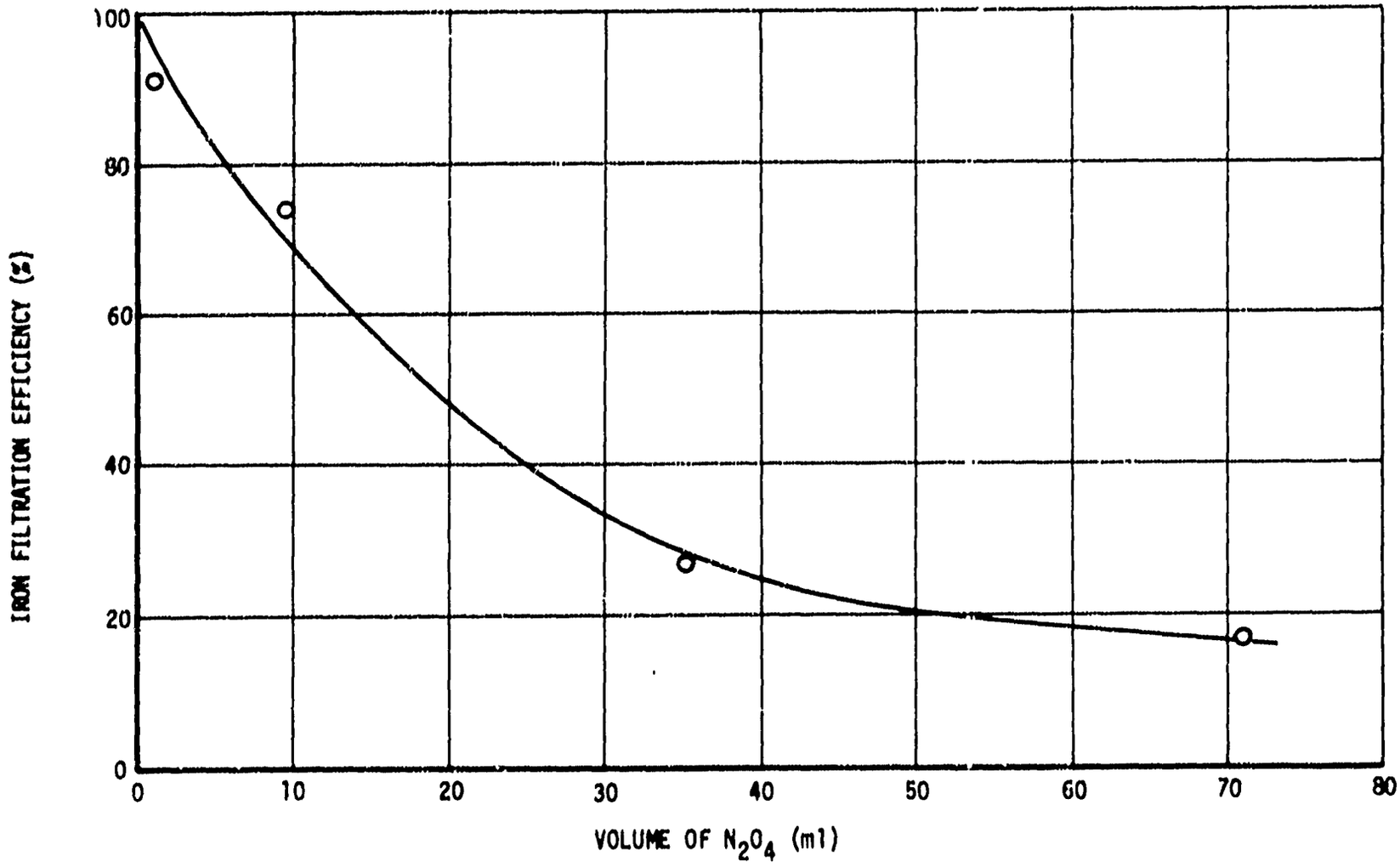
Filter Porosity (microns)	Temperature Centigrade	Filter Efficiency percent
coarse (40-60)	23	25
coarse	0	22
coarse	-10	28
fine (4-5.5)	23	63
fine	0	81
fine	-10	76

The abcve results indicate that temperature has little, if any, influence on filtration efficiency and that the fine frit was considerably more effective than the coarse as a means of removing iron. The fact that the surface area of the fine frit was relatively large suggested that surface adsorption of iron compounds might be the dominant filtering mechanism. If the active adsorption sites were quickly saturated, the filtration efficiency would be expected to diminish rapidly. The hypothesis was checked by flowing additional portions of N_2O_4 through a fine frit. A rapid decrease in filtration efficiency was in fact observed as shown in Figure 4. Small sintered glass filters were thus seen to be inadequate for removing significant quantities of iron from N_2O_4.

4.2.3 Procedure for Testing 2 Micron Stainless Steel Screen Filter

Past tests with green N_2O_4 (MSC-PPD-2A) had shown that 2 micron nominal, stainless steel, screen-type filters described previously could remove at least some of the complexed iron[7]. Consequently, it was decided to test the effectiveness of such a filter with brown NTO. A new test system adapted to this piece of hardware was assembled as shown in Figures 5-7. In this instance a stainless steel cylinder was used to supply about 80 c.c. of Fe^{59} tracer-labeled NTO which in turn passed through an aluminum coiled-tube heat exchanger at -10°C, the stainless screen filter, and into the counting containers.

FIG. 4 ILLUSTRATION OF HOW THE FILTRATION EFFICIENCY OF AN ADSORPTIVE FILTER DECREASES AS THE ACTIVE SITES ARE EXHAUSTED



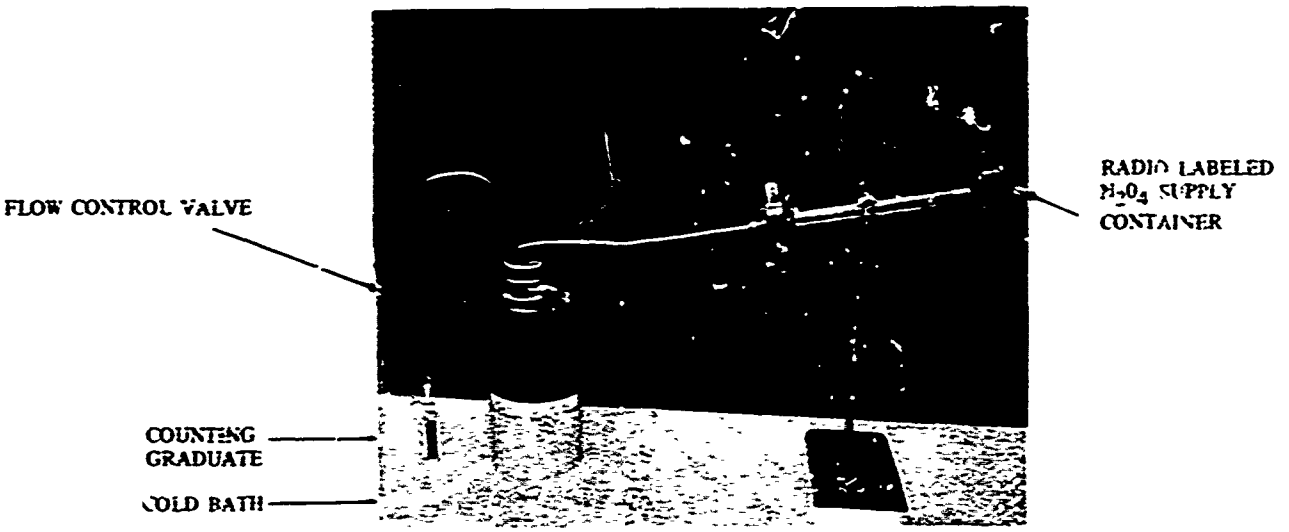


FIGURE 5. FLOW SYSTEM FOR TESTING STAINLESS STEEL SCREEN FILTERS

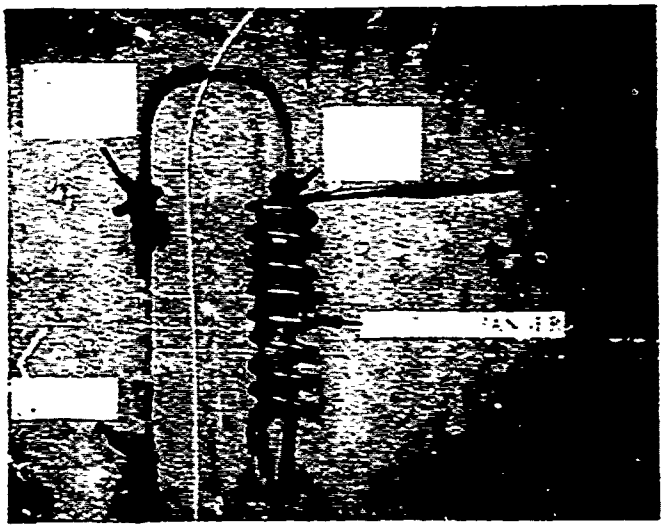


FIGURE 6. HEAT EXCHANGER AND COUNTING GRADUATE

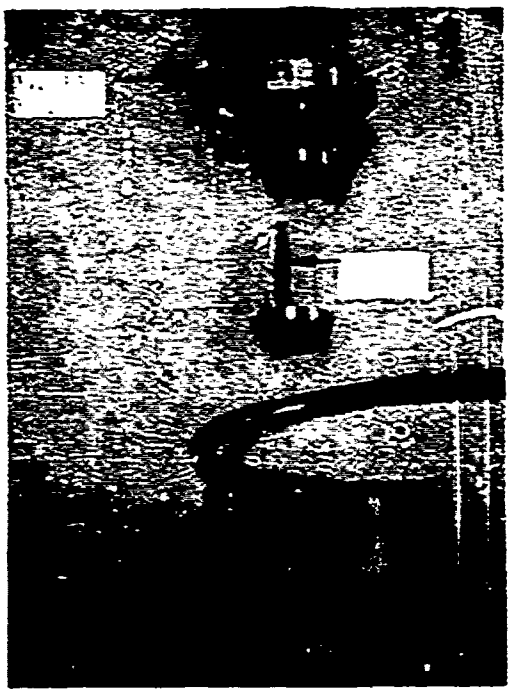


FIGURE 7. FILTER INSTALLATION

The as-received filter was cleaned by soaking in a 50-50 solution of concentrated nitric acid and water for 15 minutes, rinsed with deionized water for 2 minutes and allowed to soak in deionized water for 30 minutes. The filtration system was then evacuated for about 30 minutes with a roughing pump.

4.2.4 Results of Filtration Through a Stainless Steel Screen Filter

The observed filtration efficiencies at conditions which enhance filtration were disappointingly low. The average filtration efficiency was found to be ~14% with the passage of only 80 c.c. of NTO and it thus appeared that there was insufficient filtering action.

4.2.5 Test of Small Adsorption Filters

At this point a reassessment of the capability of filters to remove iron from N_2O_4 was in order. The previous expectation that passing cold N_2O_4 through conventional type filters would achieve high filtration efficiencies no longer appeared promising. However, the tendency of the iron to adsorb on surfaces suggested that an adsorption type filter, constructed by packing a column with an appropriate substance, might achieve the desired results.

Powdered quartz, glass wool, and molecular sieves were considered as candidate adsorption agents. These substances are low in cost, readily available, possess high surface area to mass ratios, and are inert to N_2O_4. Glass wool was tried first and performed reasonably well. A small column was tightly packed with 0.6 g of glass wool through which 63 ml of N_2O_4 was passed. Filtration efficiencies were checked at 20 ml intervals. The first 20 ml portion yielded a value of 99.9%, the second decreased

somewhat to 96.5%, and the third indicated that substantial amounts of iron had passed (filtration efficiency, 69%) for an overall efficiency of 88.5%. An important criterion of effectiveness is the ratio of the mass of N_2O_4 passed through the column (until the column begins to lose effectiveness) to the mass of the packing material. In this case these figures were about 60g of N_2O_4 compared to 0.6g of glass wool for a ratio of 100. This is an acceptable ratio for many applications, but an even higher ratio would be more desirable.

Type 13X Linde molecular sieves (chosen because this type possesses a large pore size) were studied next and these proved to be extremely effective. Previous work[8] had shown that trace metal contaminants could be removed by molecular sieves. However the bulk filtering capacity and post-filtering particulate count were not determined. In the laboratory experiment which demonstrated the feasibility of removing iron by filtration, type - 13X pellets were ground in a mortar and pestle to a coarse powder. This was performed under dry nitrogen to preclude the adsorption of atmospheric water vapor by the sieve material. A small amount of powder (.073 gm) was then transferred to a 3mm glass tube, small plugs of glass wool being used to retain the .35" long column of powder. A series of 5 c.c. volumes of Fe^{59} tracer-labeled N_2O_4 was passed through the column and each was counted to determine the amount of iron remaining in the sample. Test results were translated into overall filter efficiency (average over the entire run) as a function of the filter to N_2O_4 mass ratio and are shown in Figure 8. Estimates based on these results were made for a filter twice as long and are also included in this graph. Excellent filtration efficiencies appear possible for mass ratios in excess of 1000.

Having demonstrated a successful filtration technique for purifying N_2O_4 other questions were considered. For example the question could be raised as to whether the radio-tracer

iron was removed in a different manner than the iron which was normally present in the N_2O_4. Experiments had been performed with sintered glass filters in which radioactivity and atomic absorption spectroscopy measurements verified similar filtration removal of both kinds of iron by glass frits. However the same result would not necessarily be true for molecular sieves. In addition there were uncertainties as to whether sieve particles would be picked up from the filter and whether water might not be extracted from the sieve material by the N_2O_4.

4.2.6 -Test of an Operational Model Adsorption Filter

The very encouraging results achieved in the laboratory with type 13X molecular sieves justified a larger scale filtration test. Consequently, a filter was designed that could conceivably be useful in field operations and also permit the identification of the interaction of sieve materials with the N_2O_4, should any exist.

No detailed parametric analysis of the filter was attempted although experience gained in lab experiments was useful. For example, 1/16" diameter pellets had been found to allow channeling of the fluid around the pellets which resulted in a reduced filter efficiency. On the other hand the filter surface area could be increased by grinding the pellets to such a very fine powder that N_2O_4 would not flow through. Thus, by judgement, a filter matrix particle size was selected that would be fine enough to provide adequate adsorption area and coarse enough to permit reasonable fluid flow. Samples of 13X sieves are shown in Figure 9.

The operational size filter was a 3/4 inch O.D. type 5052 flared aluminum tube about 30 inches long, provided with

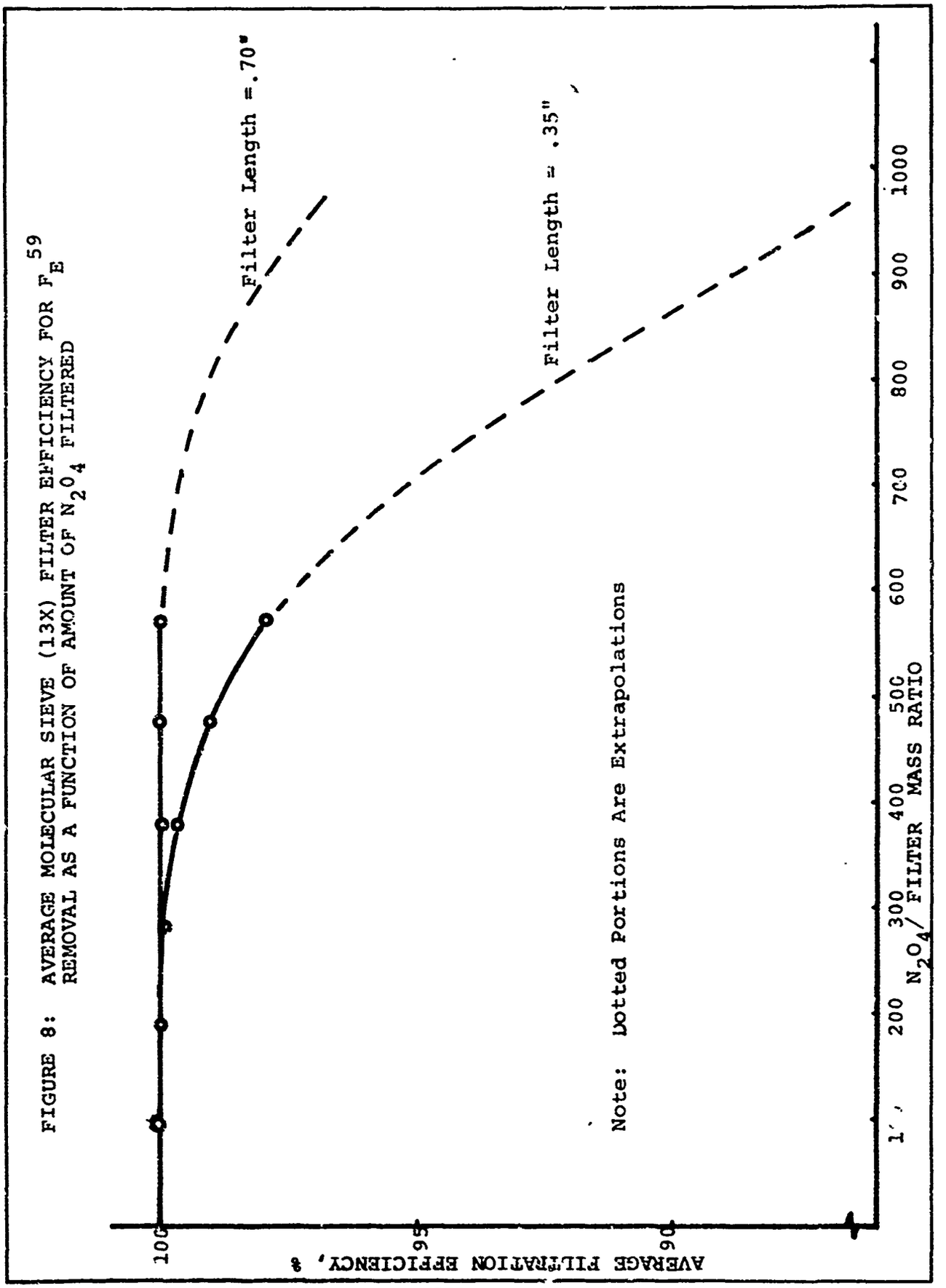


FIGURE 8: AVERAGE MOLECULAR SIEVE (13X) FILTER EFFICIENCY FOR F_E^{59} REMOVAL AS A FUNCTION OF AMOUNT OF N_2O_4 FILTERED

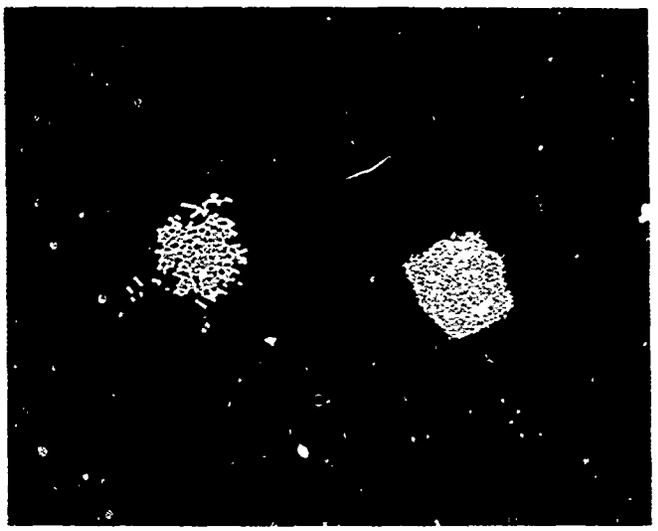


FIGURE 9. SAMPLES OF 1/16" DIAMETER AND 100/120 MESH TYPE 13 X MOLECULAR SIEVES

FIGURE 10. OPERATIONAL MODEL ADSORPTION FILTER

standard 3/4" flare fittings and, packed with 0.2 pound of type 13X Linde molecular sieves. The sieves were of chromatographic grade (Tyler standard 100/120 mesh) supplied by Coast Engineering Laboratories, Gardena, California. The sieves were retained on the inlet side by a 1/4" plug of glass wool and on the outlet side by a (2 micron nominal, 10 micron absolute) stainless steel filter supplied by Western Filter Company (part number S12-19310-2). The operational filter construction is illustrated in Figure 10.

The flow system in which the filter was tested is shown schematically in Figure 11 and photographically in Figure 12.

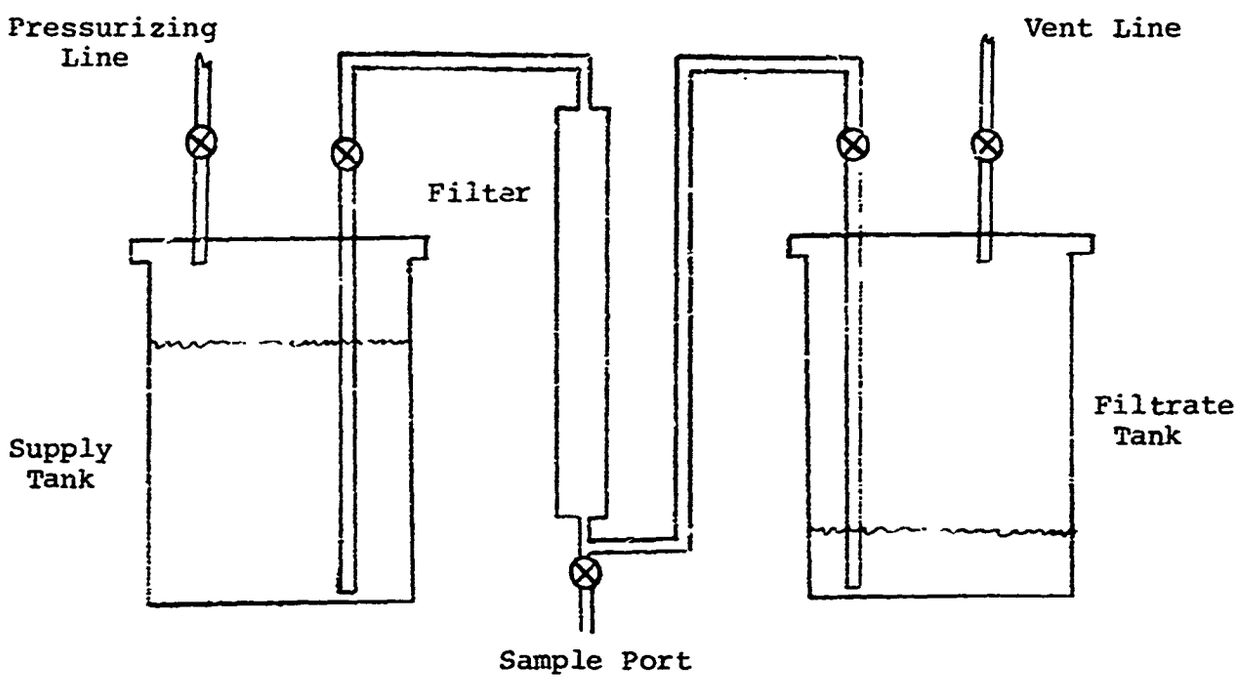


Figure 11 - Operational Filter Flow Test Schematic

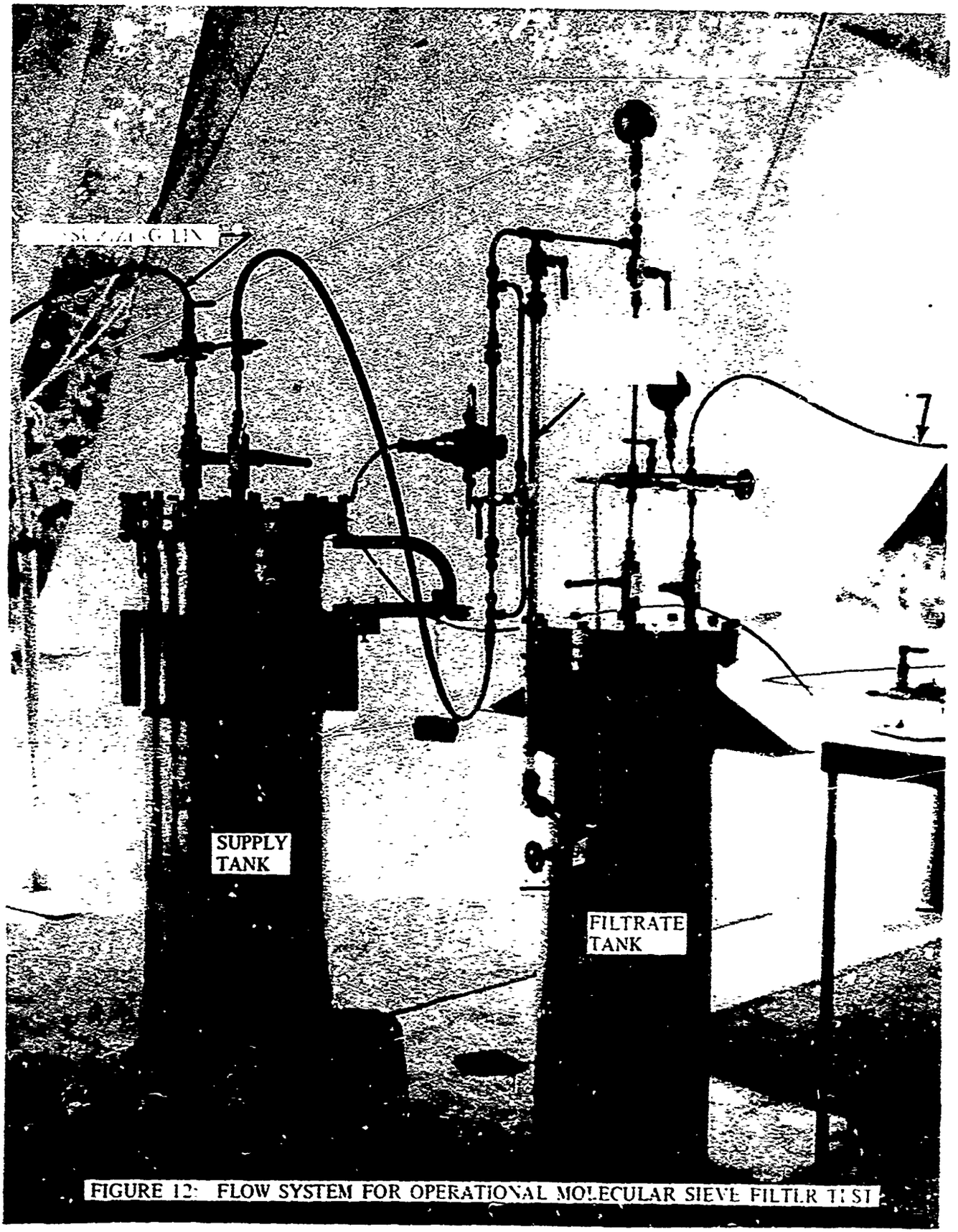


FIGURE 12: FLOW SYSTEM FOR OPERATIONAL MOLECULAR SIEVE FILTER TEST

The operational filter was connected between two 14 gallon tanks in such a way that N_2O_4 samples could be withdrawn through the sample port at any time during flow. Approximately 200 pounds was passed through the molecular sieve filter and filtrate samples were collected at 18 pound intervals. The supply tank was pressurized at 40 psig but the flow rate was limited to about .7 lb/min because of the resistance of the packed column. The filtrate samples were analyzed by atomic absorption spectroscopy to verify that the iron normally contained in the N_2O_4 was removed by the sieves as efficiently as the radio-tracer iron added during laboratory experimentation was. Results indicated in Table 2 were consistent with the results obtained in the laboratory. Virtually no iron was detected in the samples collected, the instrument readings being at the lower detection limit of the instrument. The N_2O_4 to molecular sieve mass ratio (200 lb./.2 lb) was 1000 but the capability of this particular geometry of filter may well be higher. The first sample collected (not passed through the filter) contained .46 ppm iron, a value somewhat less than a previous analysis of .55, but compatible with the accuracy of the atomic absorption instrumentation.

TABLE 2
MOLECULAR SIEVE FILTRATION RESULTS

Sample	Condition	Iron Found (PPM)	Approx. Sample Filtration Efficiency (%)
1	Not filtered (feed tank)	0.46	-
2	Filtered	0.03	94
3	Filtered	0.02	96
4	Filtered	0.01	98
5	Filtered	0.03	94
6	Filtered	0.03	94
7	Filtered	0.03	94
8	Filtered	0.02	96
9	Filtered	0.01	99
10	Filtered	0.01	98
11	Filtered	0.02	96

The filtered N_2O_4 was analyzed by standard techniques to ensure that it still met specifications, and the results are given below:

Constituent	Spec. Limits (MIL-P-26539C- Composition NTO)	Not Filtered	Filtered
N_2O_4 (%)	99.5 min.	99.86	99.8
H_2O (%)	0.17 max.	0.018	0.018
Cl (%)	0.040 max.	0.011	0.004
Particulate (mg/l)	10 max.	Not Determined	9.28

The above data shows that the filtered N_2O_4 was well within specifications. In comparison with the unfiltered propellant, the N_2O_4 assay and water content were essentially unchanged, and the chloride value was substantially reduced. Also encouraging was the low particulate matter content, which indicated that molecular sieve fines had not contaminated the propellant.

In summary, the operational, Linde type 13X, molecular sieve filter has successfully and efficiently removed iron contaminants from N_2O_4 without causing deviation from specification. The N_2O_4 molecular sieve mass ratio was 1000 and the filtration capacity was not reached.

4.3 COMPARISON OF PURIFICATION METHODS

Having demonstrated that high and low pressure distillation and filtration thru molecular sieves were all technically feasible methods of removing iron from N_2O_4 it remained to compare them from an operational standpoint. For this comparison the indices of operational attractiveness were taken to be (1) reliability, (2) effect on system readiness, and (3) cost. Since field conditions, support facilities and readiness requirements are widely variable it is meaningful to make only broad comparisons.

In general, reliability is increased by reducing the number of active elements within the system. Distillation requires a heat source, heat exchanger, condenser, coolant, coolant pumps, fluid pumps and pumping power. In contrast filtration requires only a passive filter, fluid pumps and pumping power. On this basis filtration is seen to be more attractive. Distillation at a pressure of 1 atm (coolant temperature = 21°C) is likewise preferable to low pressure distillation since a low temperature coolant is eliminated which may be difficult to provide in some cases.

It is conceivable that purification procedures could be adopted so that neither filtration or distillation would materially affect the (rocket) system readiness. For example, rather than distilling or filtering a tank of N_2O_4 into another equivalent container (which would disable the rocket system) N_2O_4 could be pumped from the bottom of the tank thru the purification components and returned to the top of the tank. With minimal axial propellant mixing this procedure would eliminate the need for an auxiliary tank and provide essentially continuous readiness. When the iron concentration of the N_2O_4 was known to be

approaching a value that would produce flow decay the purification process would be implemented. In this way the iron content of the N_2O_4 would never approach an undesirable level. From this standpoint filtration and distillation are equivalent.

The cost of either purification system is the sum of the costs of energy, hardware, required facility modification, training of operating personnel and other such factors. Most of these are indeterminant until a specified installation can be analyzed. However it can be ascertained that the energy costs of the distillation process are a few tenths of a cent per pound of N_2O_4 and that the sieve costs are comparable. The remainder of the cost factors appear substantially smaller for the filtration system.

5.0 CONTAMINATION OF N_2O_4 BY DISSOLUTION OF TANK METALS

Samples of three metal alloys, 347 stainless steel, 6Al-4V titanium, and 2014 aluminum were immersed in iron-free specification grade brown N_2O_4 and the rate of dissolution of iron from the metals was measured as a function of dissolution time, surface-to-volume ratio, state of agitation and temperature. This was accomplished by activating coupons of these metals in a thermal neutron flux of $3X10^{12} n/cm^2$ sec for 10 hours ($Fe^{58} + n = Fe^{59}$), immersing the coupons in N_2O_4 and measuring the level of activity of radioactive Fe^{59} in the N_2O_4 after the coupons are removed. From the knowledge of the ratio of radioactive to non-radioactive iron atoms, the iron concentration in parts per million (ppm) was then calculated.

In the case of the aluminum and titanium alloys no iron could be detected in the activated metal coupons. The gamma spectra did, however, show traces of other elements. These elements were not identified in the case of the titanium alloy (due to the difficulty of analyzing overlapping spectra) and appeared to be chromium and zinc in the case of the aluminum sample. Consequently, emphasis was placed on the 347 stainless steel tests.

5.1 Test Procedure

Two mil 6Al-4V titanium foil, 20 mil 2014 aluminum sheet and 1 mil 347 stainless steel foil were purchased from commercial vendors. In addition a piece of 347 stainless steel bellows from the post boost propulsion system (PBPS) of Minuteman III was procured. Prior to the neutron irradiation these were cut into suitable coupons, cleaned and sealed in polyethylene containers.

The cleaning procedure for the 347 stainless and 2014 aluminum consisted of a 15 minute immersion in trichloroethylene at room temperature, 15 minute immersion in Ivory detergent solution at 50°C, 10 minute immersion in a 50/50 solution of concentrated nitric acid and water at room temperature and a final 10 minute rinse with flowing demineralized water. Solutions were agitated during immersion. The 6Al-4V titanium cleaning procedure was similar except that the initial immersion used acetone instead of trichloroethylene.

Twenty-five (25) gram samples of specification grade brown N_2O_4 were distilled into glass tubes to remove residual iron. Each aliquot of N_2O_4 was loaded into the glass container by distilling to dryness, thus ensuring that the concentrations of volatile impurities such as H_2O, NO, and NOCl were kept

constant and equal to the concentrations in the as-received N_2O_4. With an irradiated metal coupon sealed into each tube and with the N_2O_4 frozen the container was evacuated and the vacuum connection fused closed. The N_2O_4 was then allowed to come to room temperature.

Immersions were performed by allowing the N_2O_4 to run to the end of the tube containing the metal coupon as shown in Figure 13. Following the prescribed immersion the liquid was drained back into the far end of the glass tube (See Figure 14)which was then inserted into the radioactivity counting equipment.

Agitation of the tubes during dissolution was provided by a magnetic stirrer. A 1" diameter glass tube containing a stirring bar was attached to the lower end of the tube (or tubes) requiring agitation which were supported near the upper end. Motion of the stirring bar caused deflections of this cantilever beam arrangement which resulted in appreciable sloshing of the N_2O_4 around the metal coupons.

One elevated temperature dissolution was made. The temperature was stabilized at 47°C by means of a constant temperature bath which corresponds to a typical hot day, and fluctuated about this point within 1/2°C during the course of the test.

The equipment used in counting is shown in Figures 15 and 16. The end of the glass tube containing N_2O_4 was placed in a lead shield which contained a 3" x 3" cylindrical sodium iodide crystal. Gamma rays given off by the decay of iron-59 interacted in the crystal to produce flashes of light whose intensity was a function of gamma energy. These in turn were sensed by a photomultiplier tube which in conjunction

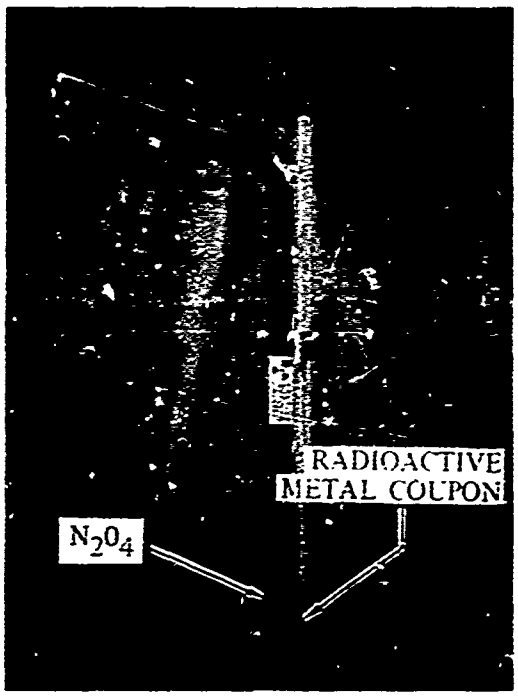


FIGURE 13. IMMERSION ORIENTATION OF DISSOLUTION TUBE

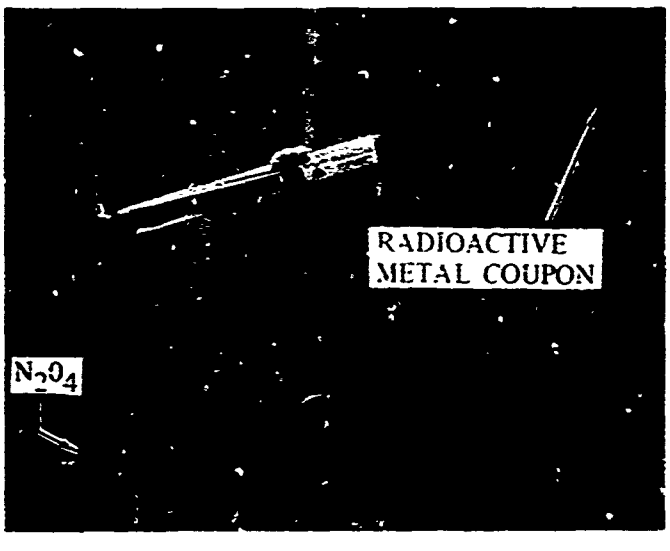


FIGURE 14. COUNTING ORIENTATION OF DISSOLUTION TUBE

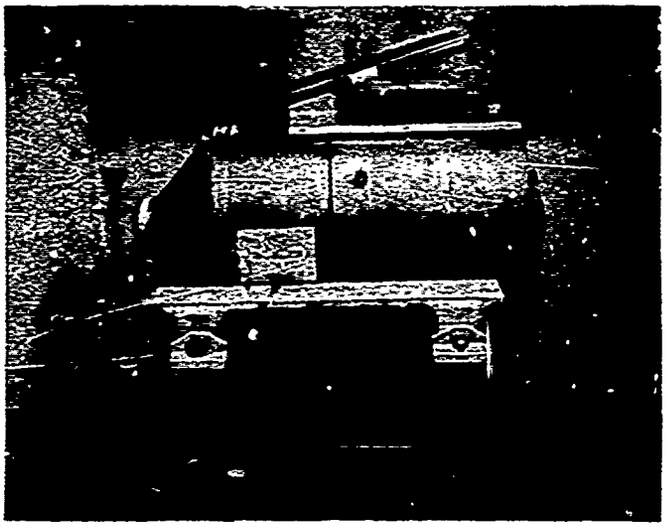


FIGURE 15. TUBE IN COUNTING SHIELD

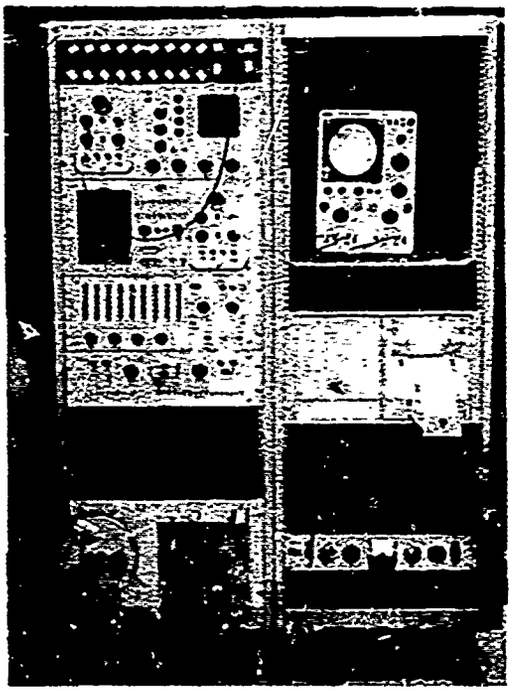


FIGURE 16. COUNTING EQUIPMENT

with other electronics counted the pulses, sorted the energies and stored the data. The data could then be printed out on paper tape. Each isotope has characteristic energy spectra which could be used to identify and quantify the isotope.

5.2 Results of Dissolution Tests

The results of the 347 stainless steel (PBPS bellow samples) dissolution tests are summarized in Figures 17, 18. It is observed that the rate of dissolution is apparently independent of agitation. That is, the tube which was allowed to stand undisturbed contained as much iron as the one which was agitated.

The elevated temperature test indicates a modest increase in the rate of iron dissolution when immersed at 47°C for 2 days. After the conclusion of this test the tube was included along with several others in an extended dissolution test at room temperature. This is indicated by the dashed portion of the curve and shows an iron concentration about 3 times that of a similar tube which was always at room temperature.

Four sets of 347 stainless steel, room temperature data were collected, corresponding to four different metal surface to N_2O_4 volume ratios. The rate of iron buildup was found to level off quickly.

There is a surface area reaction rate dependence such that the higher surface areas have the higher reaction rates, although the dependence does not appear to be linear with the surface area. For example, the reaction rate $S/V = 11.4$ inch^{-1} is 4 times that of $S/V = 5.7$ inch^{-1} at 100 hr.. It is possible that the surface reaction is limited by the number of reactive surface sites available, which could vary somewhat from coupon to coupon. For example active sites could be formed

FIGURE 17 DISSOLUTION OF IRON FROM 347 STAINLESS STEEL BY BROWN NITROGEN TETROXIDE AT DIFFERENT TEMPERATURES & S/V DURING QUIESCENT IMMERSION

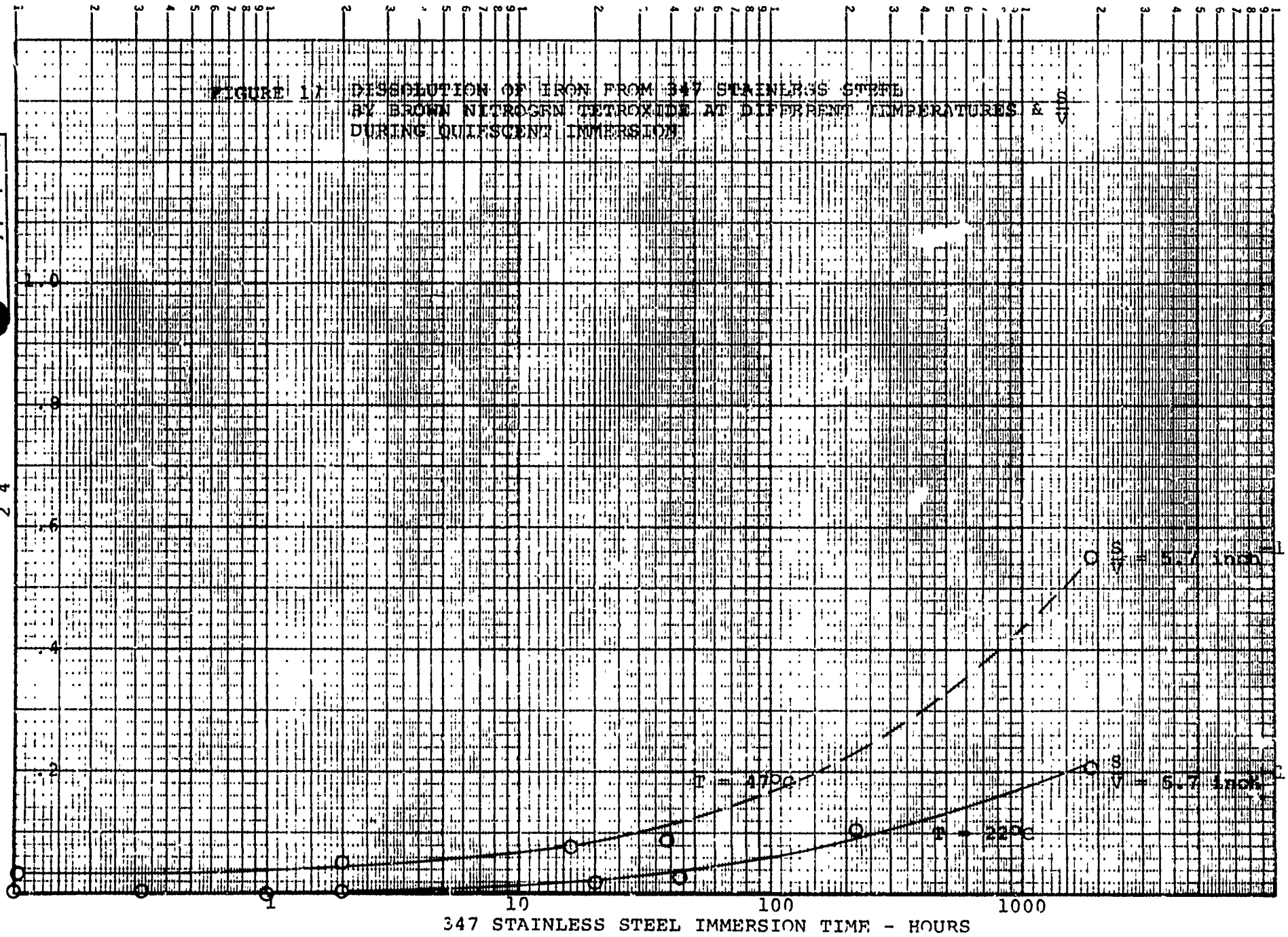
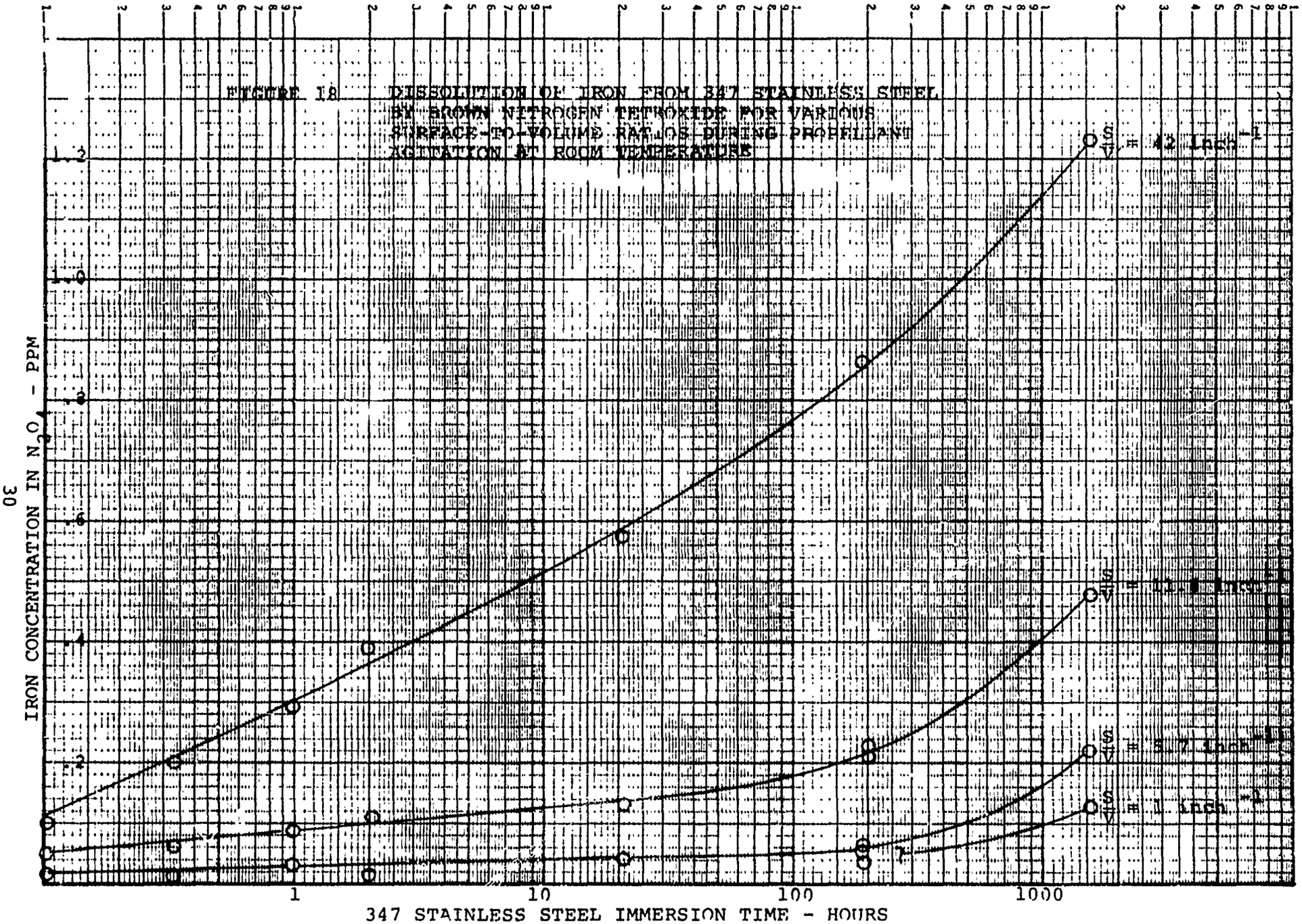


FIGURE 18 DISSOLUTION OF IRON FROM 347 STAINLESS STEEL BY BROWN NITROGEN TETROXIDE FOR VARIOUS SURFACE-TO-VOLUME RATIOS DURING PROPELLANT AGITATION AT ROOM TEMPERATURE



along the edges or corners of the coupons when cut to size. These sites might be small areas of iron or iron oxide which are not completely screened by the protective chromium oxide layer known to exist on stainless steel surfaces.

The S/V ratios of many propellant feed tanks fall in the 0.1 to 1.0 $inch^{-1}$ range and it would appear from the data generated that loading a 347 stainless steel tank with initially iron-free N_2O_4 would obviate flow decay problems, because the S/V ratio is so small that no appreciable build-up of iron would be predicted to occur even after long storage periods. This conclusion is, of course, limited by the conditions present during the test. Processing and cleaning of the metal surfaces as well as variations in the concentrations of typical impurities (such as H_2O, NO, and NOCl) could possibly have considerable effect on the rate of reaction.

One final result involved the dissolution of the titanium metal coupon. Although no iron was detected in either 6Al-4V titanium or 2014 aluminum these dissolution tubes were included with other 347 stainless steel tubes during the long immersion which was performed. Upon checking the N_2O_4 which had been in contact with titanium, significant radioactivity was observed. The element to which this activity belongs was not, however, identified due to the press of other experimental requirements and the difficulty of analyzing overlapping gamma ray spectra.

6.0 N_2O_4 FLOW TESTS

Some research workers still consider flow decay as something of an elusive phenomenon. Different conditions under which flow decay can occur have been tabulated, but there are so many possible variables (e.g., type of constriction, temperature,

pressure, flow rate, and concentrations of H_2O, NO, Cl^- and the iron nitrate complex), one must use care in interpreting flow decay data. Perhaps the most important variable is the presence of the iron nitrate complex, the removal of which forms the basis of the flow decay prevention method. The importance of determining the degree of flow decay as a function of iron concentration is quite clear, but it must be remembered that the data are applicable to the various flow conditions present in the particular flow apparatus under study.

In this study, a flow system was assembled which consisted of a 2 gallon supply tank, heat exchanger, orifice plate flow meter, fine-mesh stainless steel screen filter, flow control device and 2 gallon catch tank. A flow by-pass was placed around the filter so that the N_2O_4 could be transferred back to the supply tank from the catch tank without back flushing the filter. The N_2O_4 from the supply tank was cooled to 0°C in the heat exchanger prior to passage through the filter with the intent of inducing flow decay by clogging of the filter. The first test objective was to establish the level of flow decay (filter clogging) as a function of the iron content of the N_2O_4.

Two methods of introducing iron to the N_2O_4 were used. In the first, known amounts of iron were added to a tank of N_2O_4 in the form of iron nitrate. In the second, iron-free N_2O_4 was stored in 347 stainless steel, 6Al-4V titanium and 2014 aluminum tanks for an extended period of time during which the N_2O_4 was allowed to react with the tank walls.

The other objective of this series of tests was to demonstrate an operational technique for eliminating flow decay under conditions conducive to its occurrence. The operational type molecular sieve filter used in previous experiments was used in this demonstration.

6.1 Development of Flow System Configuration

The initial configuration Figure 19 employed a throttling valve as the flow control device and the first test involved the flow of N_2O_4 taken from the main storage tank. Previous analyses had indicated an average iron concentration of 0.5 ppm. Passage of N_2O_4 through the filter resulted in degradation of the flow rate from 0.22 gal/min to 0.03 gal/min (Figure 20) in the course of 5 recirculations of the N_2O_4. Filter clogging was evidenced by an increase in the pressure drop across the filter. Subsequent examination of the filter revealed the presence of a substance that did not resemble a flow decay-producing iron nitrate complex, but rather a material which was stable in air. This was ascribed to sediments initially in the transfer lines from the main storage tank .

The flow system was cleaned, the stainless steel filter replaced, a 2014 aluminum tank installed as a catch tank, an on-off valve placed in series with the throttling valve and permanent plumbing added to permit recirculation of N_2O_4 from the catch tank to the supply tank, Figure 21. The initial flow rate was set at .22 gal/min with the throttling valve. Flow decay was observed immediately but there was no pressure drop increase across the filter, Figure 22. After checking the operation of the system components it was concluded that the throttling valve was clogging. Had the flow been continuous the decay could have been as much as 50%. However the valve partially unclogged during the transfer of N_2O_4 from the catch tank back to the supply tank, so that the actual decay was ~25%.

In an attempt to induce clogging in the filter the flow rate was cut in half and indeed the filter began to clog, as is evidenced by the pressure drop across the filter in pass #6 in Figure 23. This was the last run of the afternoon on

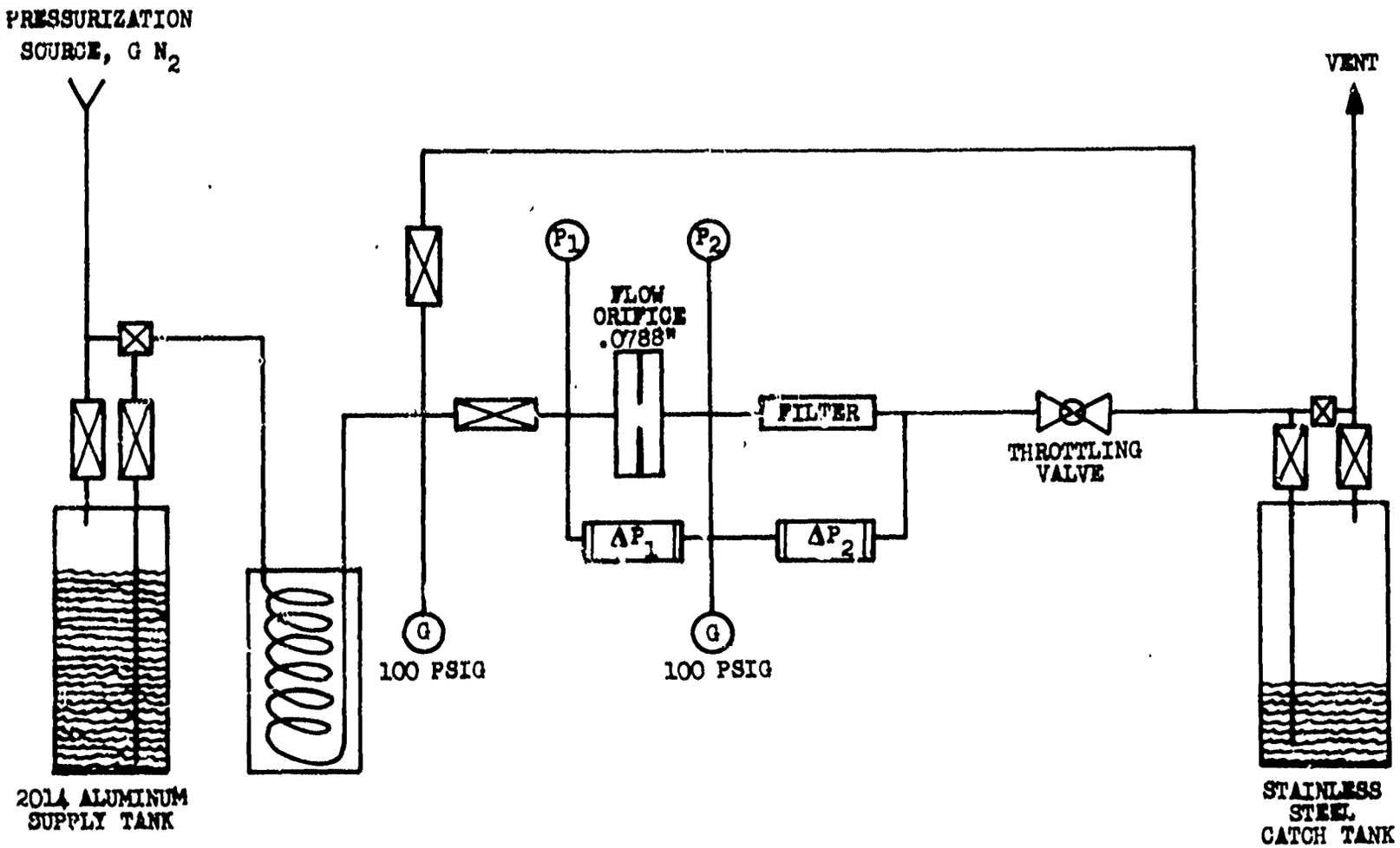


Figure 19 : INITIAL N_2O_4 FLOW TEST SCHEMATIC

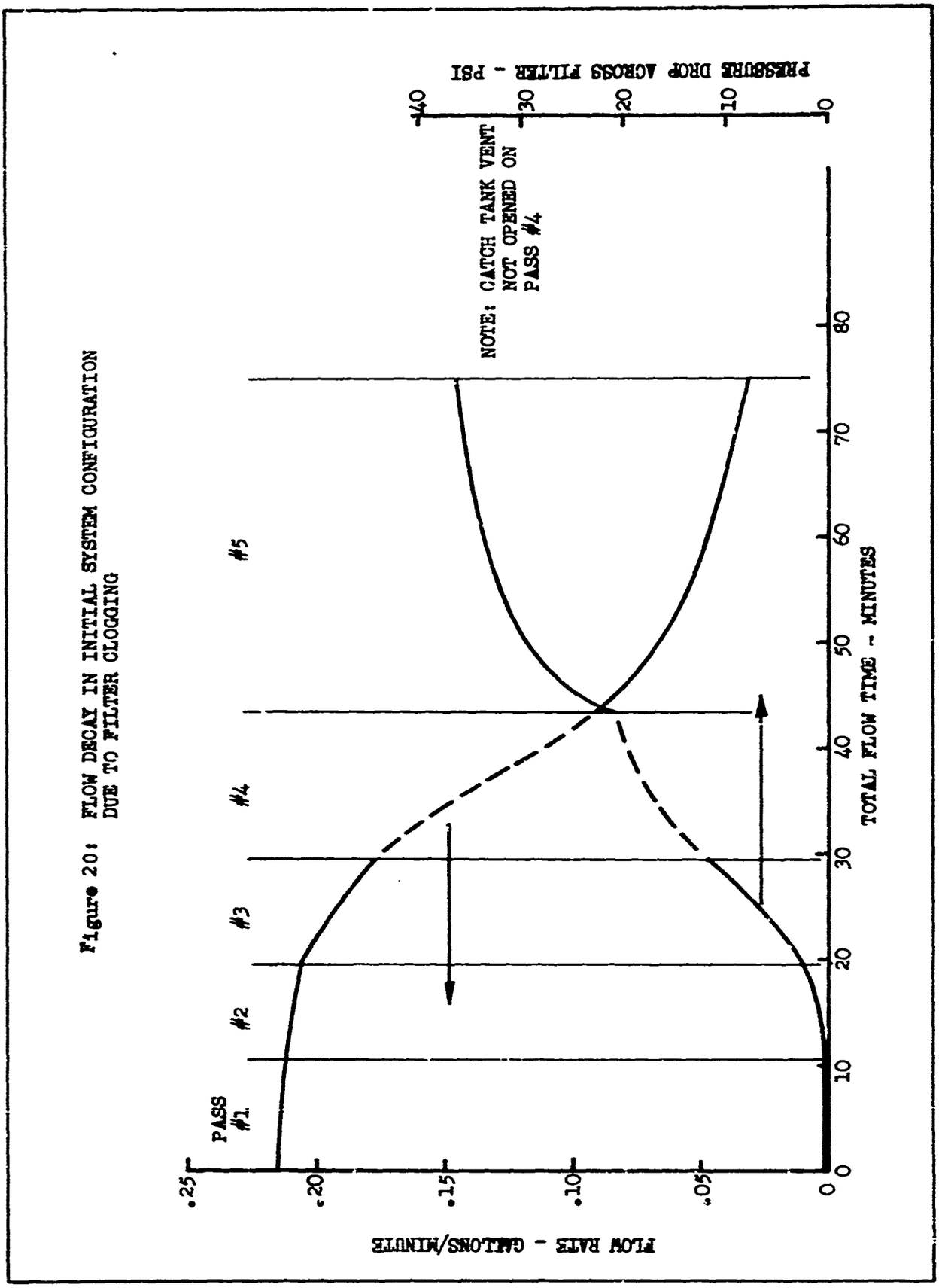


Figure 20: FLOW DECAY IN INITIAL SYSTEM CONFIGURATION DUE TO FILTER CLOGGING

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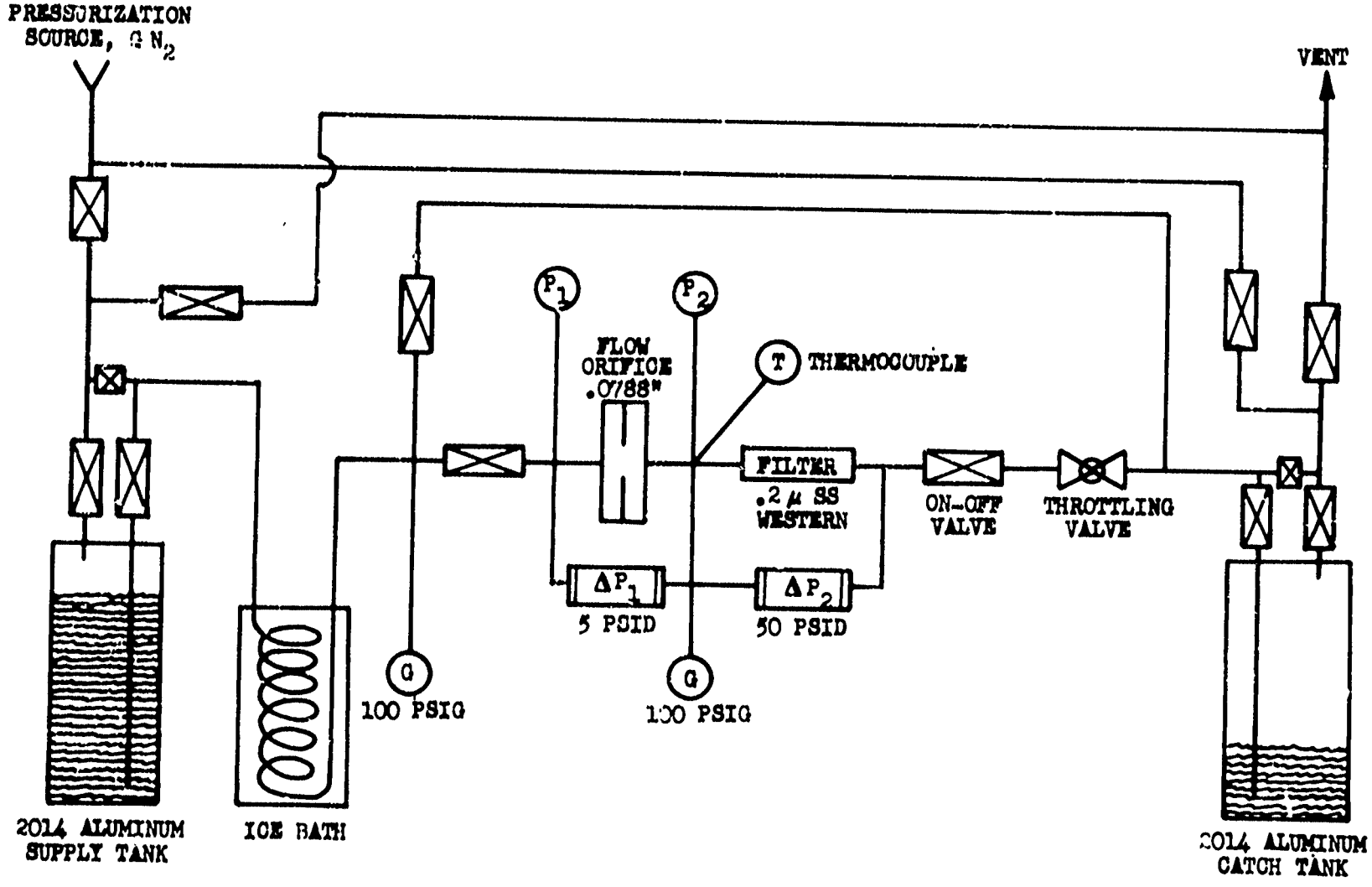

Figure 21: MODIFIED N_2O_4 FLOW TEST SCHEMATIC

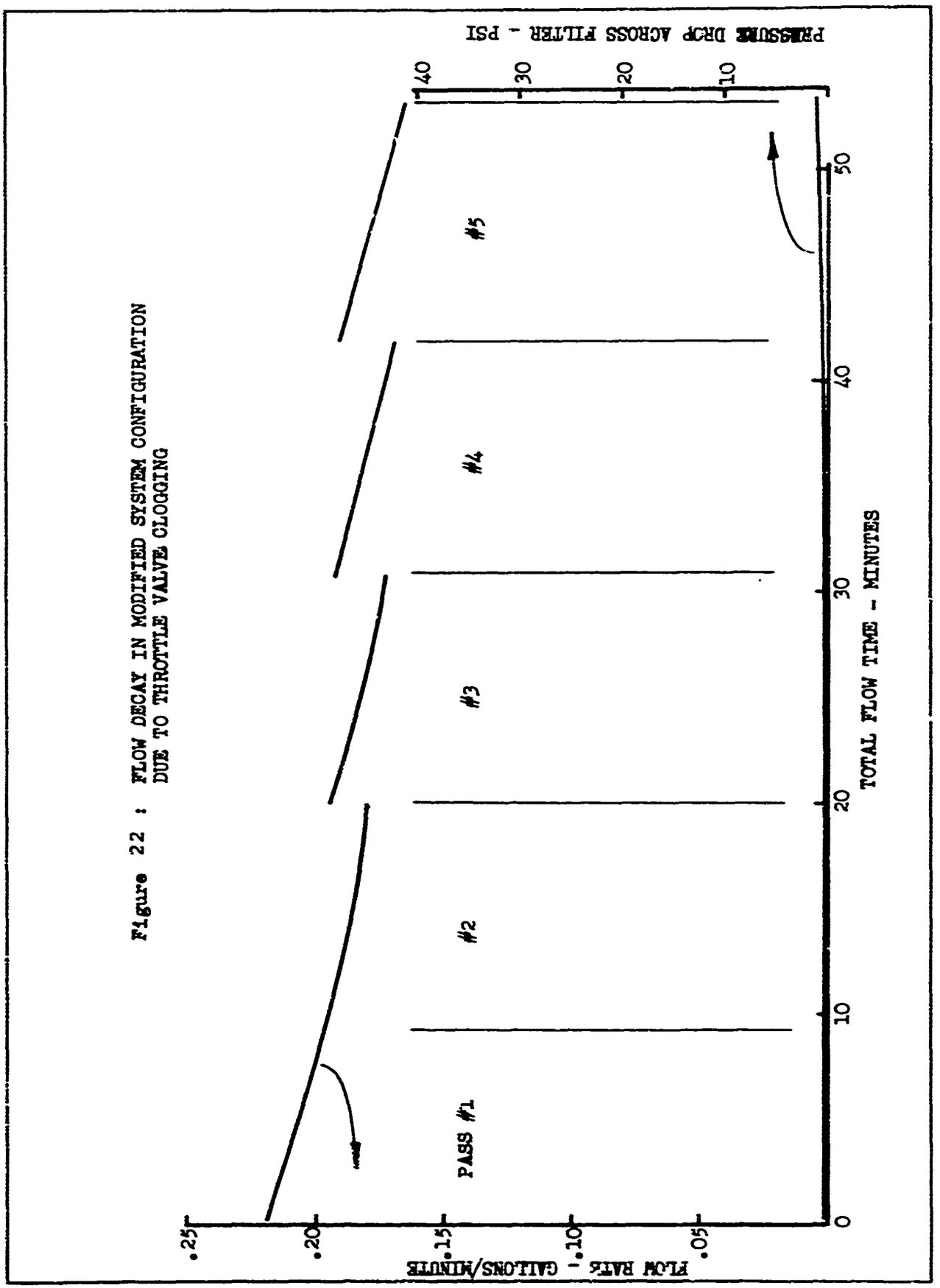

Figure 22 : FLOW DECAY IN MODIFIED SYSTEM CONFIGURATION DUE TO THROTTLE VALVE CLOGGING

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Friday, June 30, and after transfering the N_2O_4 back to the supply tank the system was valved off until the next Monday.

The first pass of that day, pass #7, at an initial flow of .11 gal/min produced no flow decay and no pressure drop across the filter. This indicates that the throttling valve and filter had been cleared of clogging elements. However, succeeding passes produced filter clogging as shown in Figure 23.

Final modifications were now made to the flow system to arrive at what is termed the "standard" flow system configuration. The throttle valve, which was susceptible to clogging, was replaced with an orifice plate containing 4-0.021" diameter holes. A differential pressure transducer was used to measure the pressure drop across the orifice plate in order to determine quantitatively the extent of clogging of the orifices. (None was detected in any of the subsequent runs.) In addition an arrangement was introduced by which the catch tank could be back-pressurized to permit variations of supply tank driving pressure while retaining a constant flow rate of approximately .2 gal/min. See figures 24, 25.

In the standard configuration the flow apparatus was constructed almost entirely of aluminum alloy. The feed and catch tanks (about 2 gallons capacity) were of type 2014 aluminum, while the lines were of 5052 aluminum. The only ferrous alloy components in the system were the valves, the filter (Western Filter Company, 2 micron nominal, 10 micron absolute, part number S12-19310-2), an eight-inch long section of 3/8-inch O.D. stainless steel tubing in which the 0.0788-inch diameter flow rate measuring orifice plate was located, and the orifice plate itself.

The feed tank was pressurized with nitrogen at 37.5-40 psig. The N_2O_4 passed through a plate containing four 0.021-inch

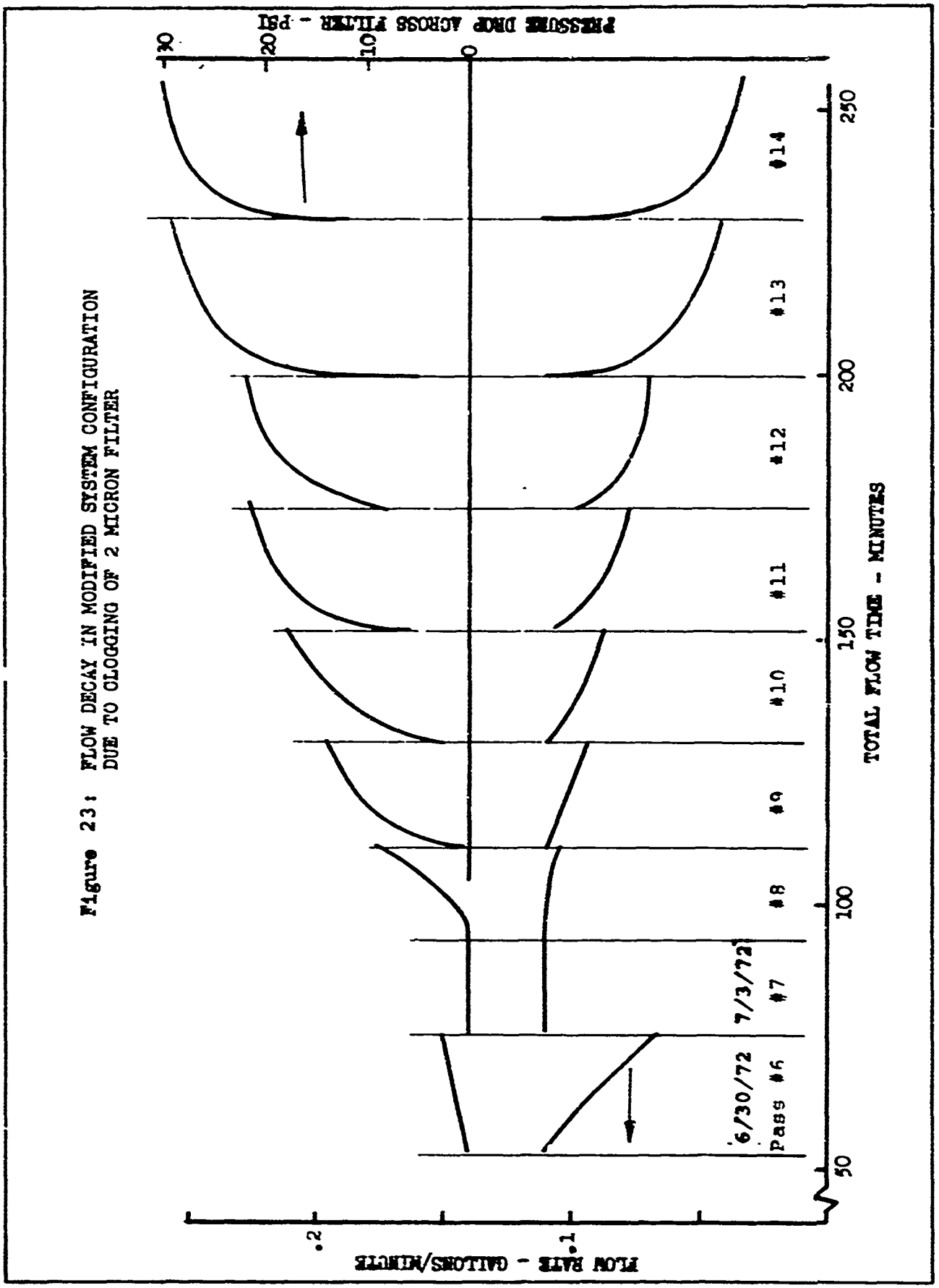

Figure 23: FLOW DECAY IN MODIFIED SYSTEM CONFIGURATION DUE TO CLOGGING OF 2 MICRON FILTER

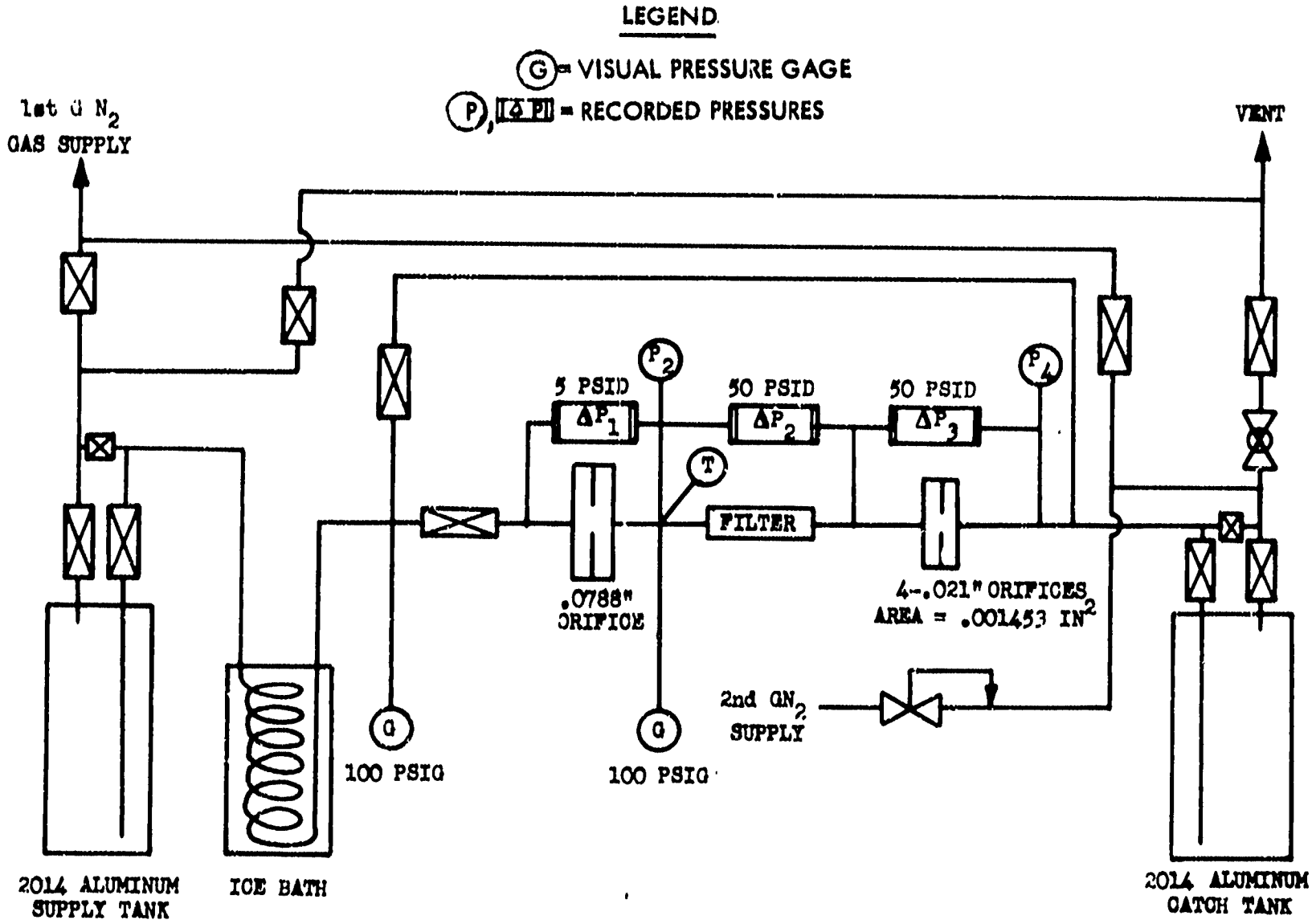

Figure 24 : STANDARD N_2O_4 FLOW TEST SCHEMATIC

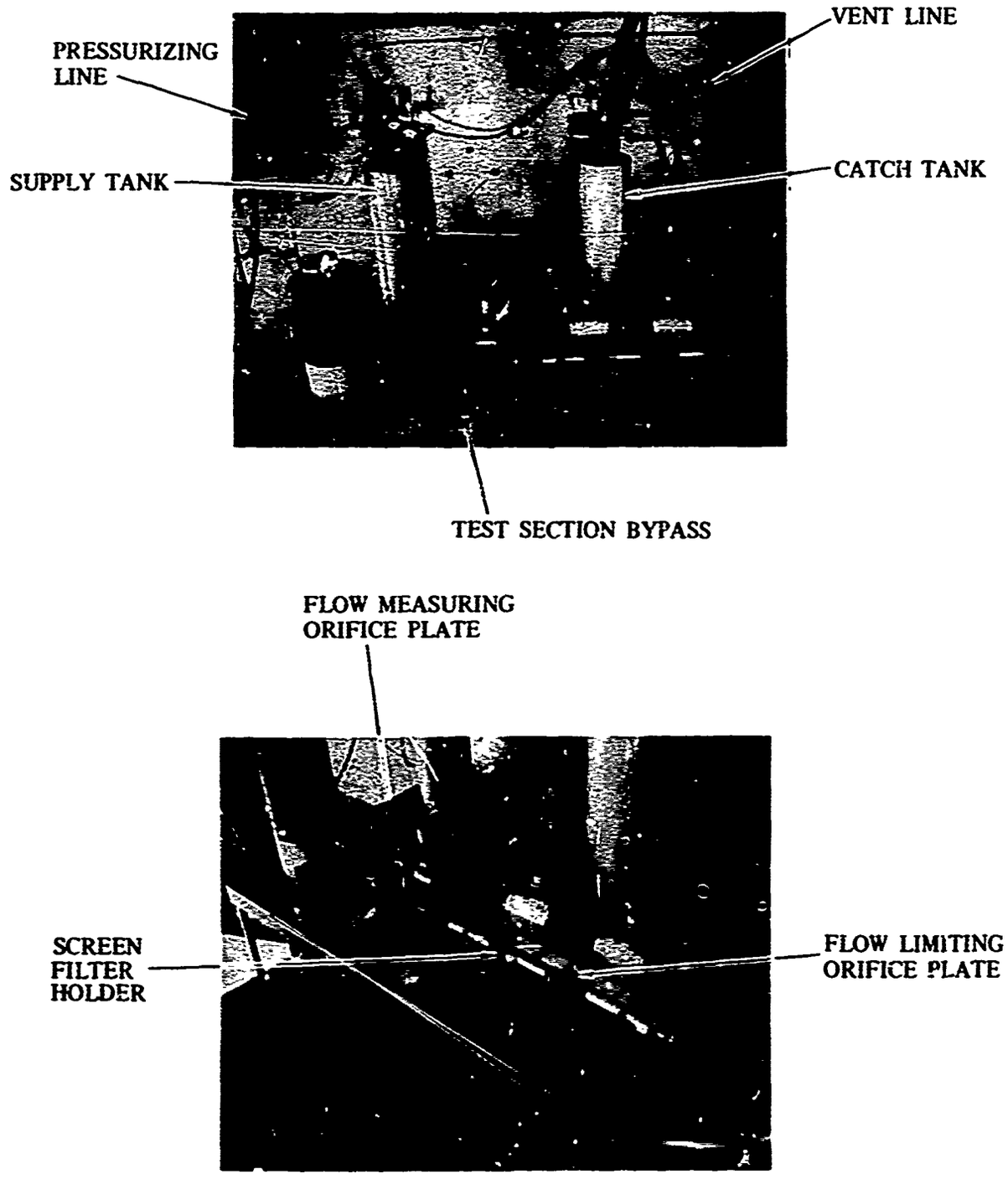

FIGURE 25. STANDARD FLOW SYSTEM HARDWARE

diameter orifices which limited flow to about 0.2 gallons per minute when the catch tank was back pressurized to 0-12 psig. Prior to reaching the test section (filter) the N_2O_4 was passed through a cooling coil held at 0°C.

6.2 Flow of As-received N_2O_4 with and without Added Iron

The first test in the standard configuration was made with a clean system, a new filter and a fresh supply tank of as-received N_2O_4 taken from the main storage tank as before. Flowing at ~.2 gal/min and even at ~.1 gal/min for several passes produced no flow decay, Figure 26. The fact that this N_2O_4, containing 0.5 ppm iron, did not exhibit flow decay was somewhat surprising since previous work at Boeing[7] had found significant flow decay at concentrations as low as 0.3 ppm. (The previous work, however, had been done with a different type of N_2O_4, "green" instead of "brown", in a different flow system (stainless steel instead of aluminum) with slightly different flow conditions.)

At this point it was decided to add additional iron to the N_2O_4 in an effort to induce flow decay. The sequence followed was to add iron in increments of 1 ppm and recirculate the N_2O_4 several times through the flow apparatus. The incremental change in iron content was achieved by adding ferric nitrate (10 mg of iron dissolved in 0.1 ml of concentrated HNO_3) to the 2 gallons (about 10^4 g) of N_2O_4. The increase in water equivalent (less than 0.001%) was considered negligible. Previous Boeing work had indicated this simple method of iron addition to be an effective means of establishing flow decay. The flow results, which ranged from no to almost complete flow decay, are best appreciated by reference to the graphs, Figures 26-31.

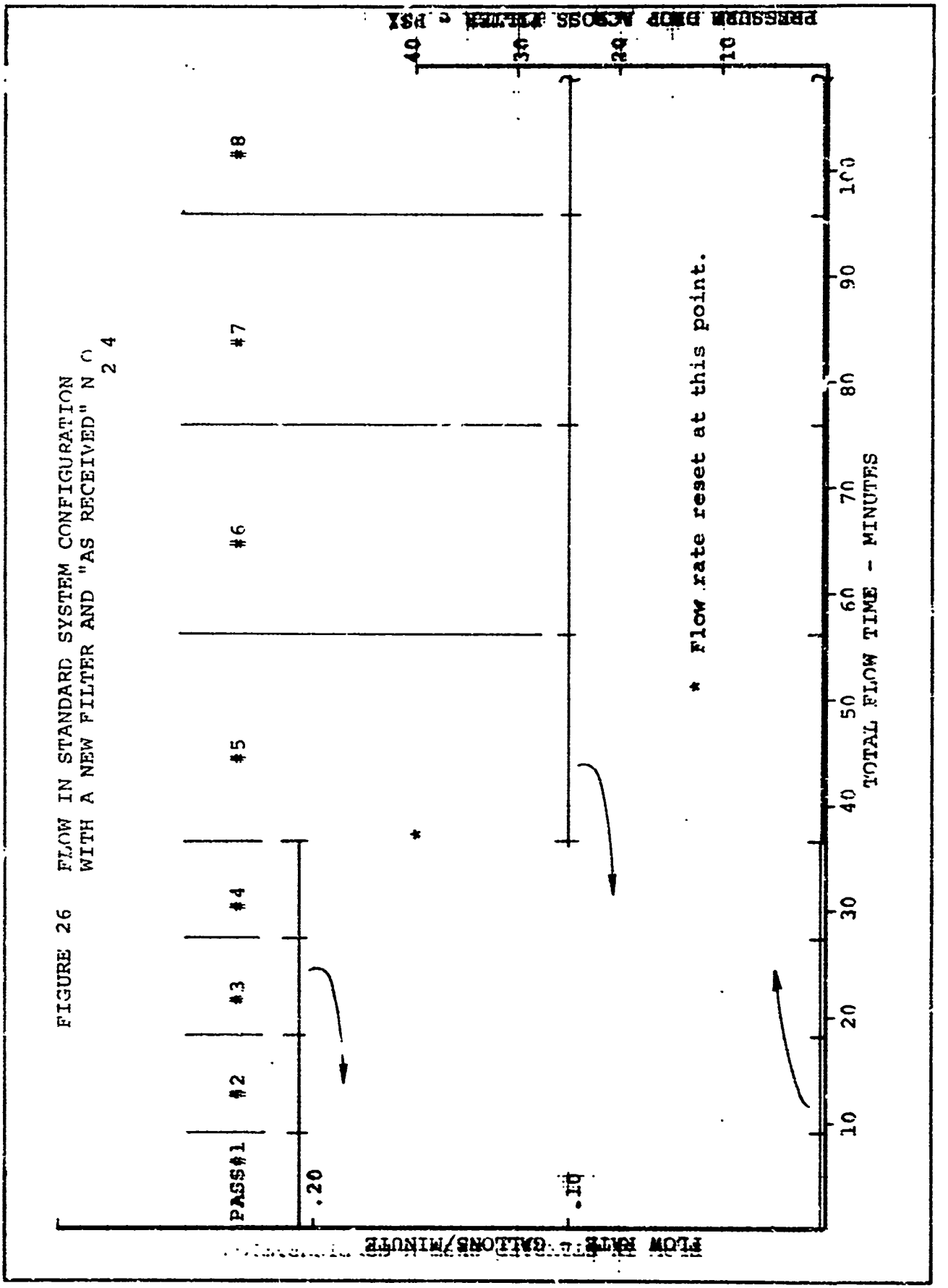

FIGURE 26 FLOW IN STANDARD SYSTEM CONFIGURATION
WITH A NEW FILTER AND "AS RECEIVED" N C
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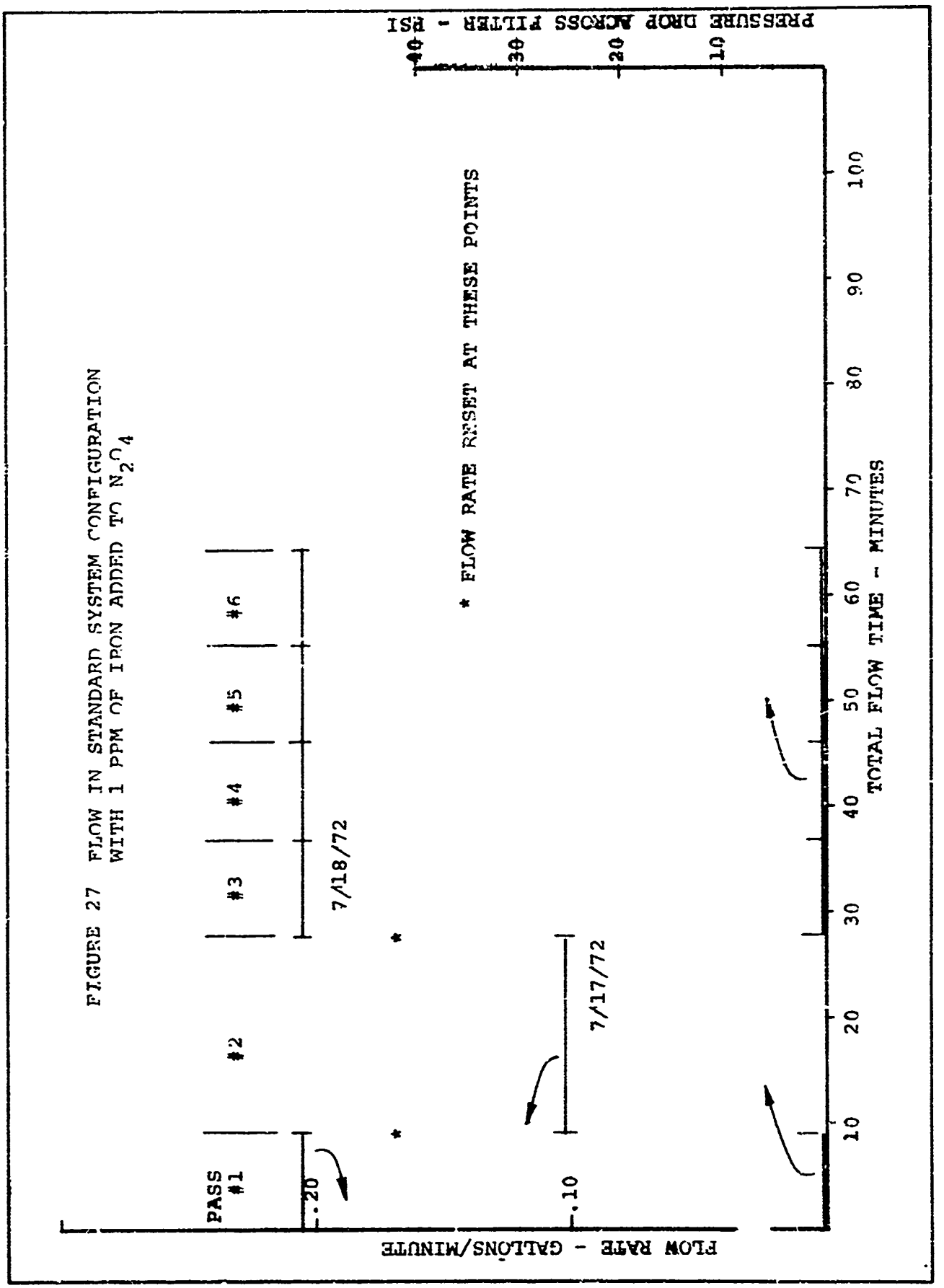


FIGURE 27 FLOW IN STANDARD SYSTEM CONFIGURATION WITH 1 PPM OF IRON ADDED TO N_2O_4

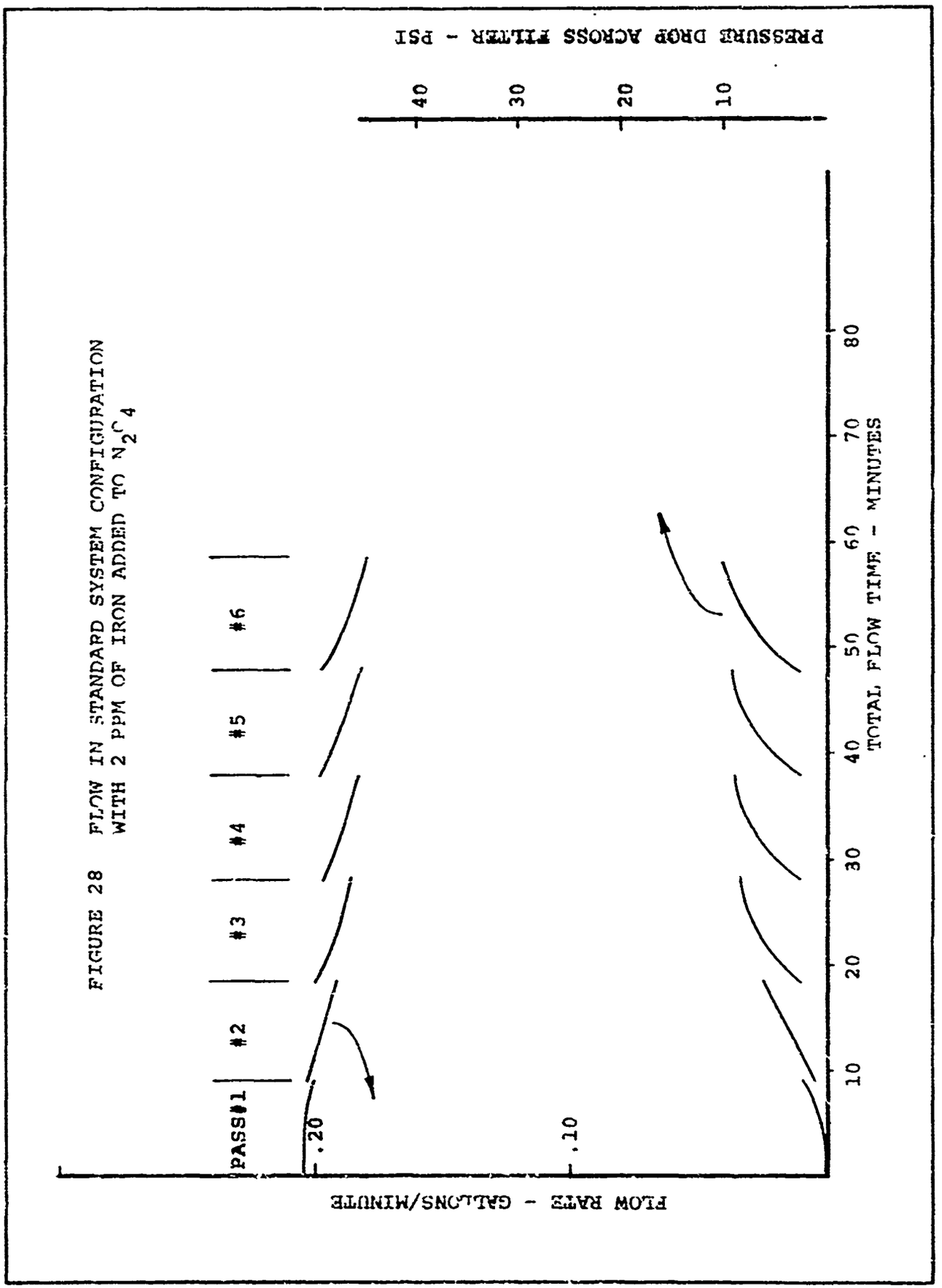


FIGURE 28 FLOW IN STANDARD SYSTEM CONFIGURATION WITH 2 PPM OF IRON ADDED TO N_2O_4

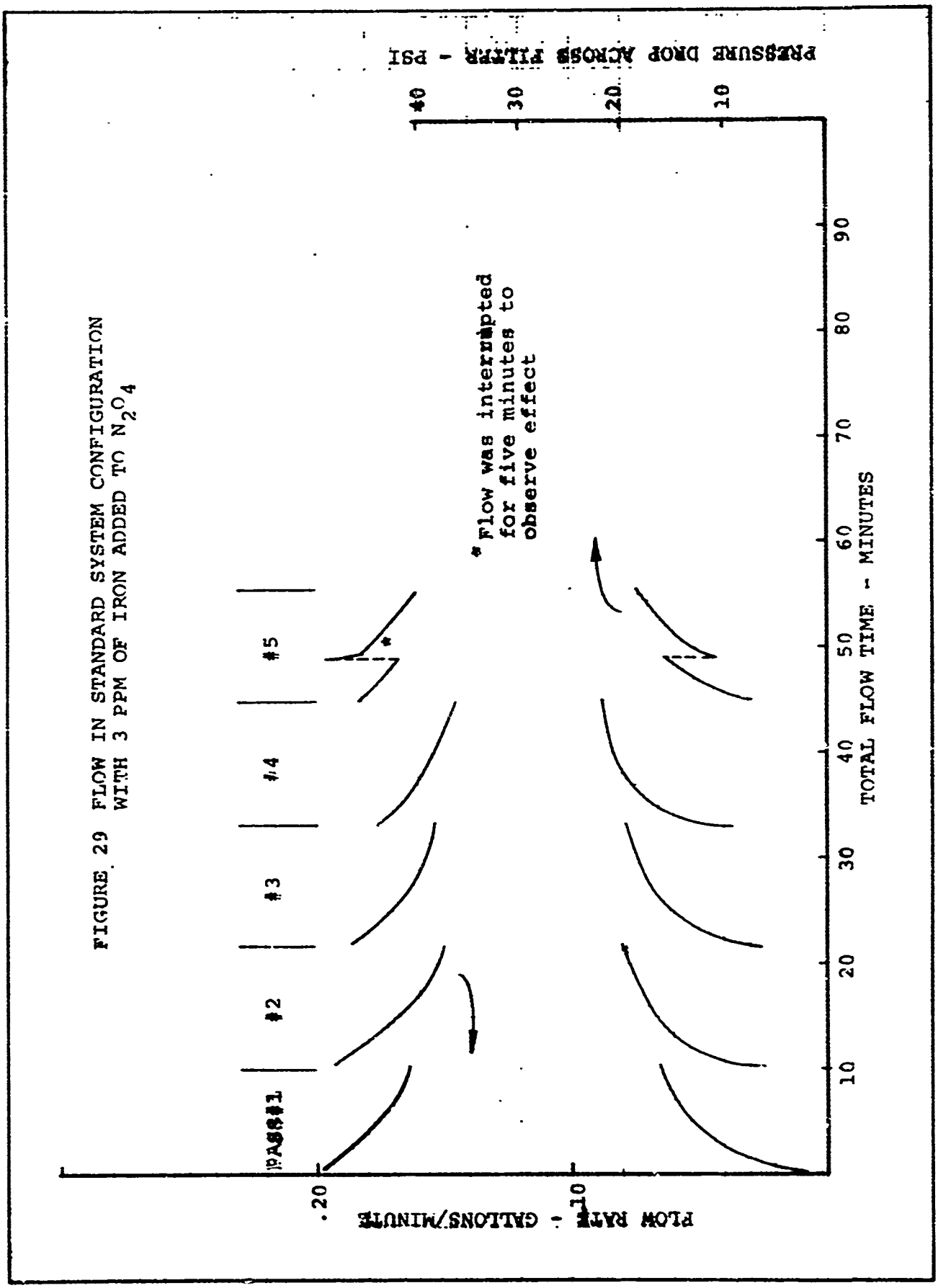


FIGURE 29 FLOW IN STANDARD SYSTEM CONFIGURATION WITH 3 PPM OF IRON ADDED TO N_2O_4

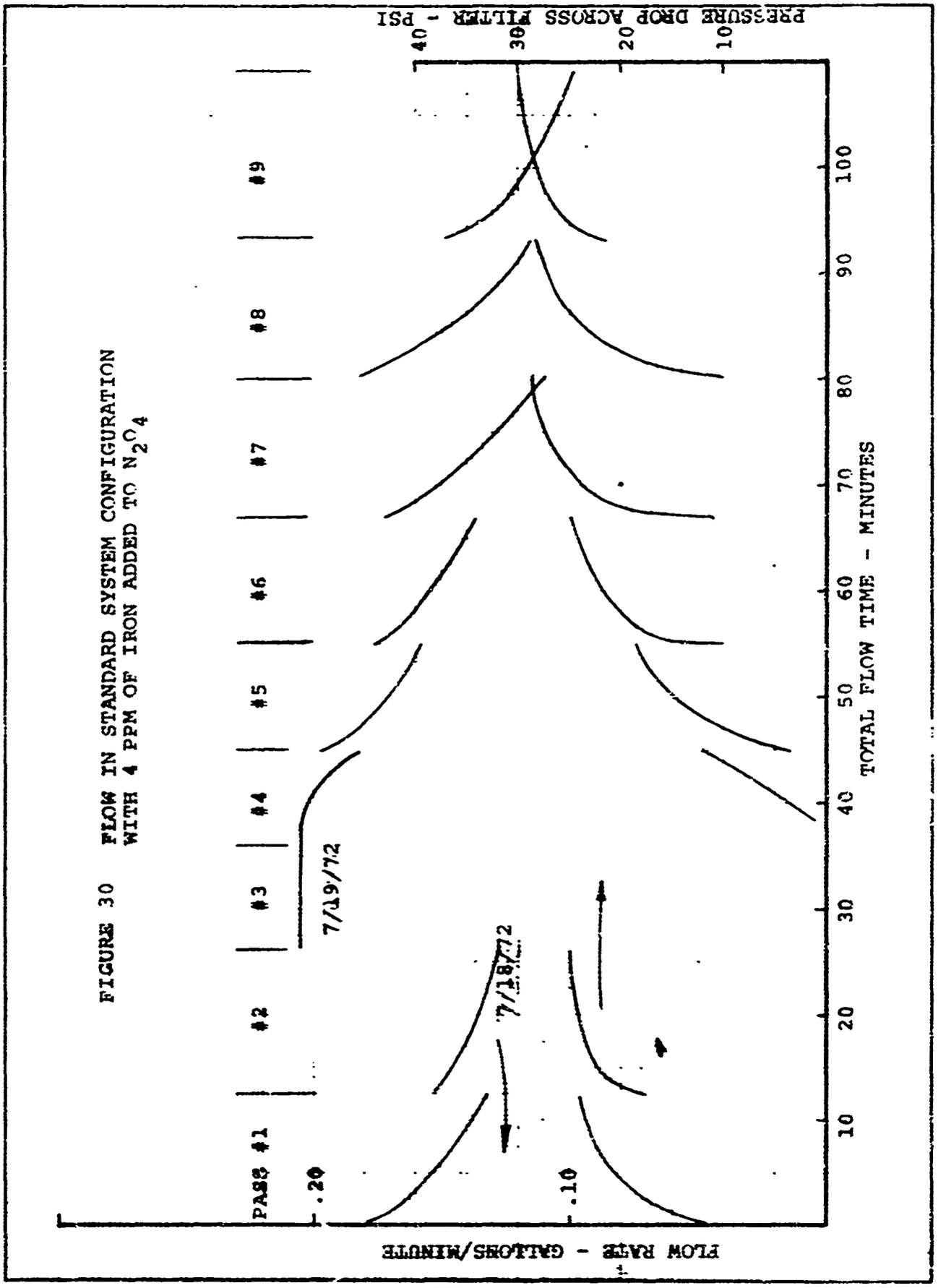


FIGURE 30 FLOW IN STANDARD SYSTEM CONFIGURATION WITH 4 PPM OF IRON ADDED TO N_2O_4

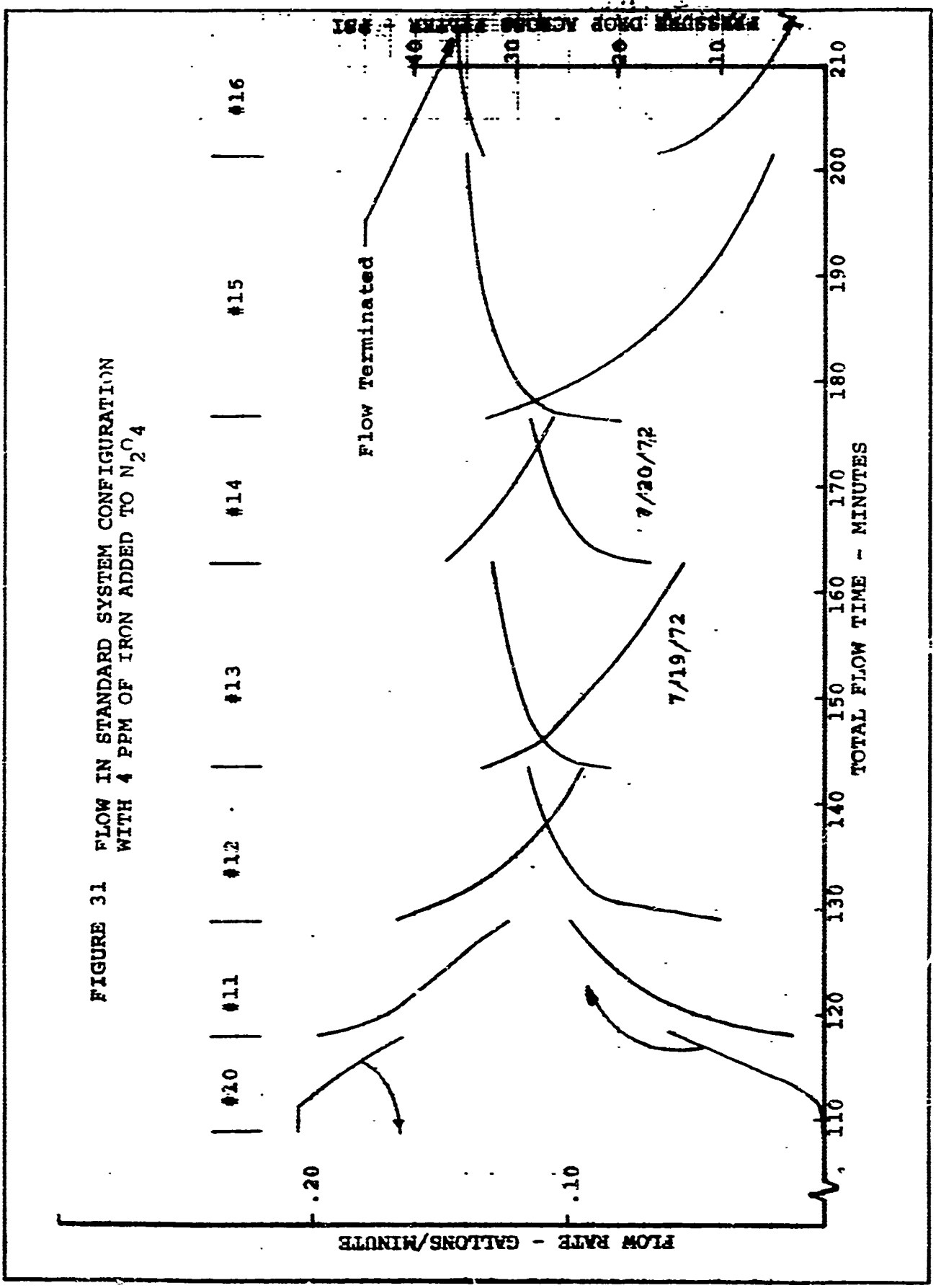


FIGURE 31 FLOW IN STANDARD SYSTEM CONFIGURATION WITH 4 PPM OF IRON ADDED TO N_2O_4

Discontinuities in flow were characteristically observed between runs in which flow decay occurred. In such cases the initial flow of a succeeding run was greater than the terminal flow in the immediately preceding one. Since there was no reverse flow in the test section, the partial clearing of the filter appears to be due to a partial reabsorption of the clogging materials by the N_2O_4.

One of the objectives of flow testing was to demonstrate elimination of flow decay with the molecular sieve filter. This was to be accomplished by flowing N_2O_4 which was known to undergo severe flow decay through the molecular sieve filter and then again through the flow system to verify that flow decay no longer occurred. Since severe decay was experienced after addition of 4 ppm iron this was the point at which the use of molecular sieve purification appeared appropriate.

Following the last recirculation of the N_2O_4 to which 4 ppm iron had been added the screen filter was back flushed so that the N_2O_4 ran from the catch tank through the filter and into the supply tank, thus tending to wash the clogging material from the filter. In the next recirculation after the flushing the initial flow rate returned to its original full scale value, (which indicates that most of the clogging material was washed back into the supply tank), and then rapidly decayed, Figure 32. With this demonstration that the clogging material could be washed back into the supply tank the back flushing operation was repeated and the N_2O_4 was then purified by passage through the molecular sieve filter. During subsequent recirculations of the purified N_2O_4 through the screen filter no flow decay was found to occur, Figure 33.

Subsequently, flowing as received N_2O_4 and as received N_2O_4 plus 1 ppm iron through this screen filter produced flow decay whereas with a clean filter it did not occur, Figures 34, 35. This suggests that some contributory flow decay factors were present, such as the filter being only partially cleaned by

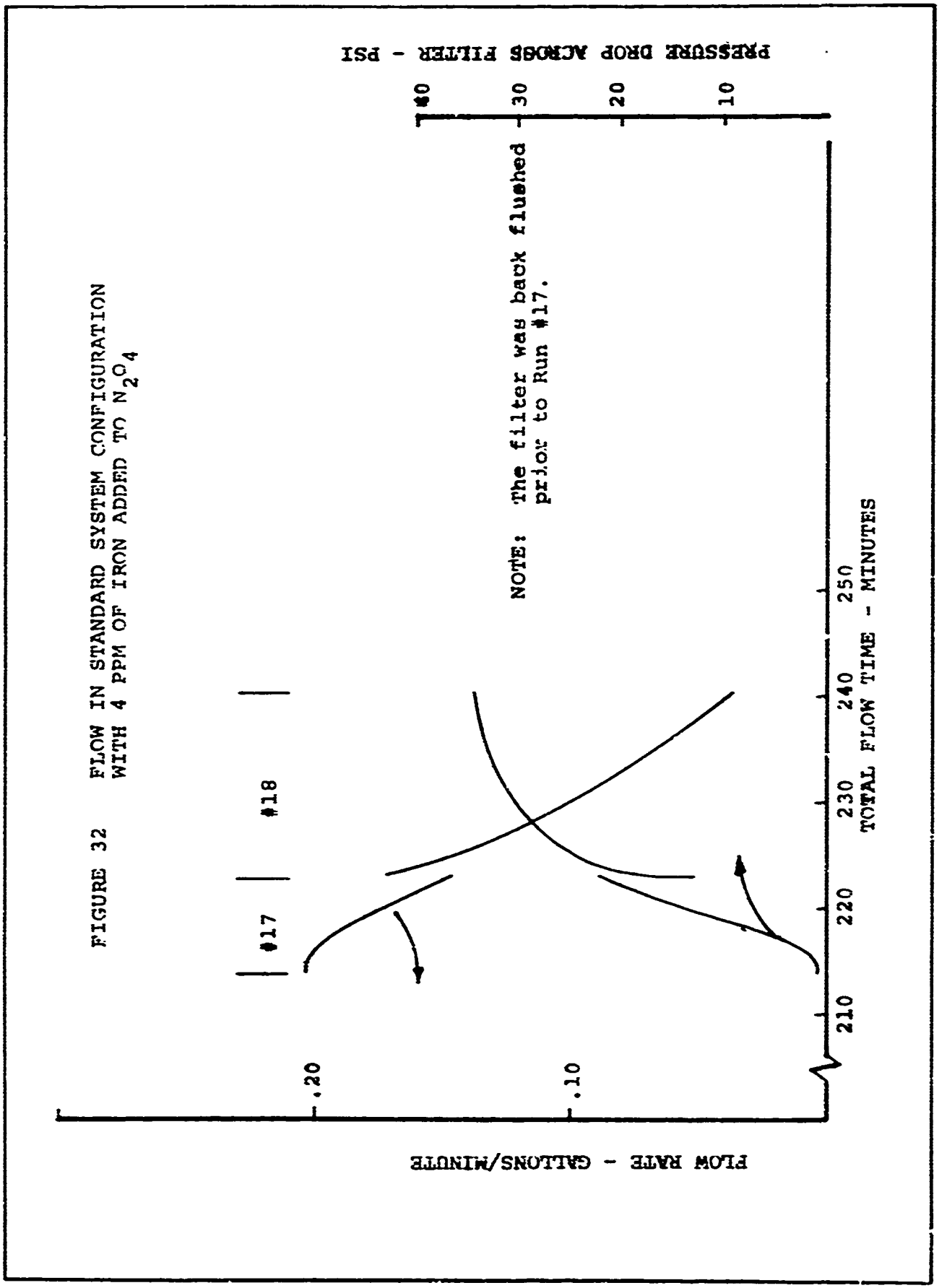
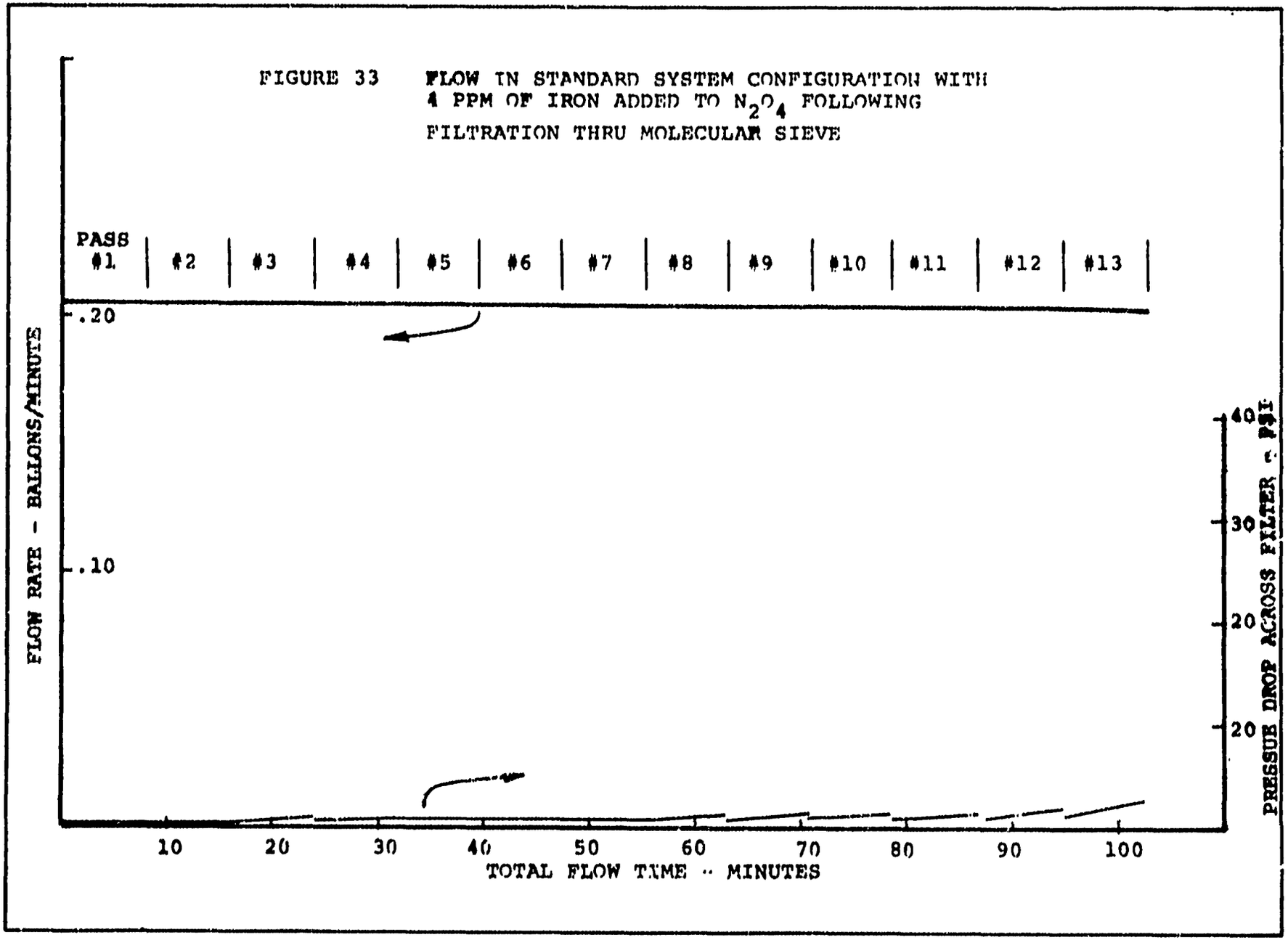


FIGURE 32 FLOW IN STANDARD SYSTEM CONFIGURATION WITH 4 PPM OF IRON ADDED TO N_2O_4

FIGURE 33 FLOW IN STANDARD SYSTEM CONFIGURATION WITH 4 PPM OF IRON ADDED TO N_2O_4 FOLLOWING FILTRATION THRU MOLECULAR SIEVE



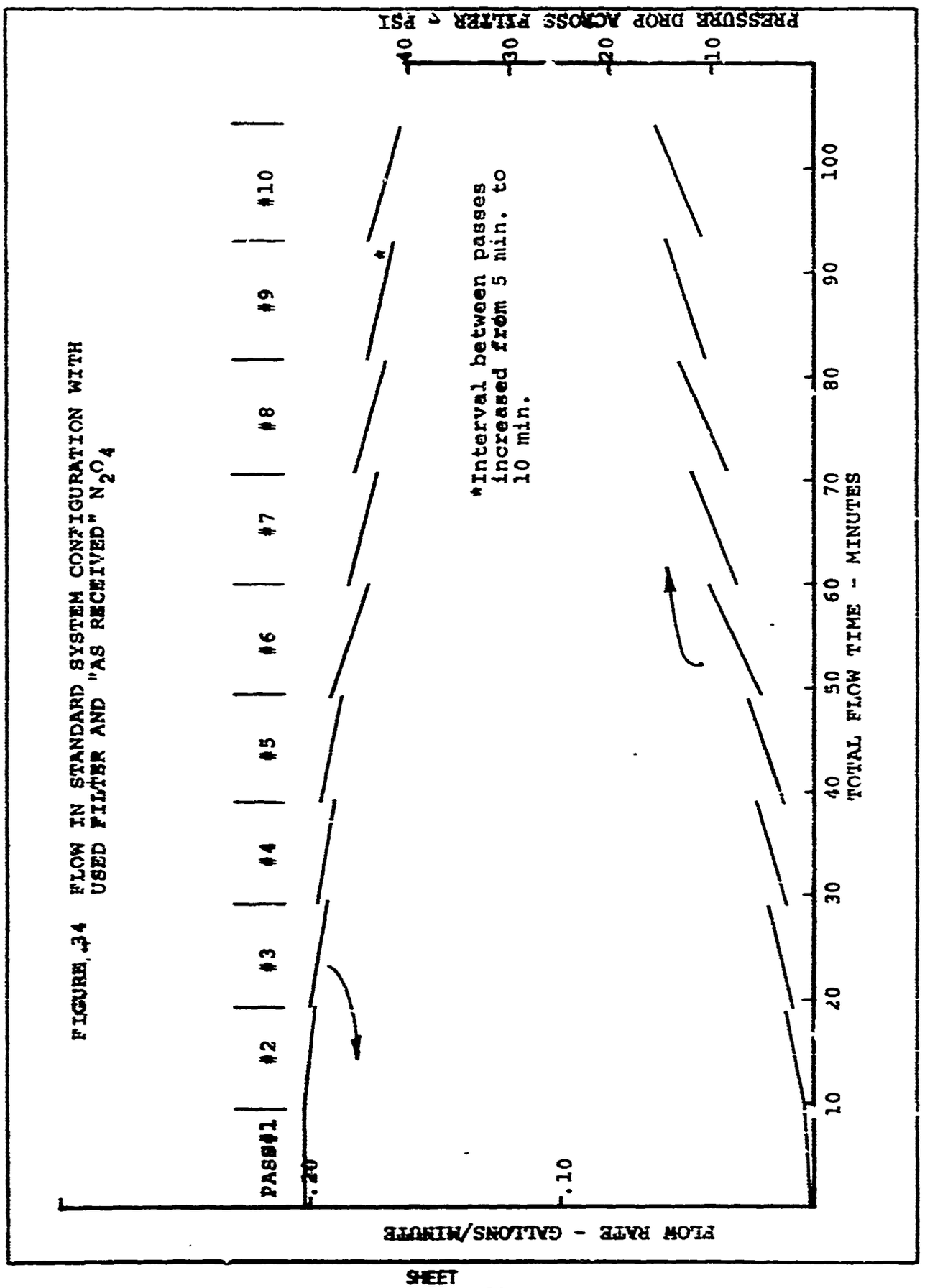


FIGURE 34 FLOW IN STANDARD SYSTEM CONFIGURATION WITH USED FILTER AND "AS RECEIVED" N_2O_4

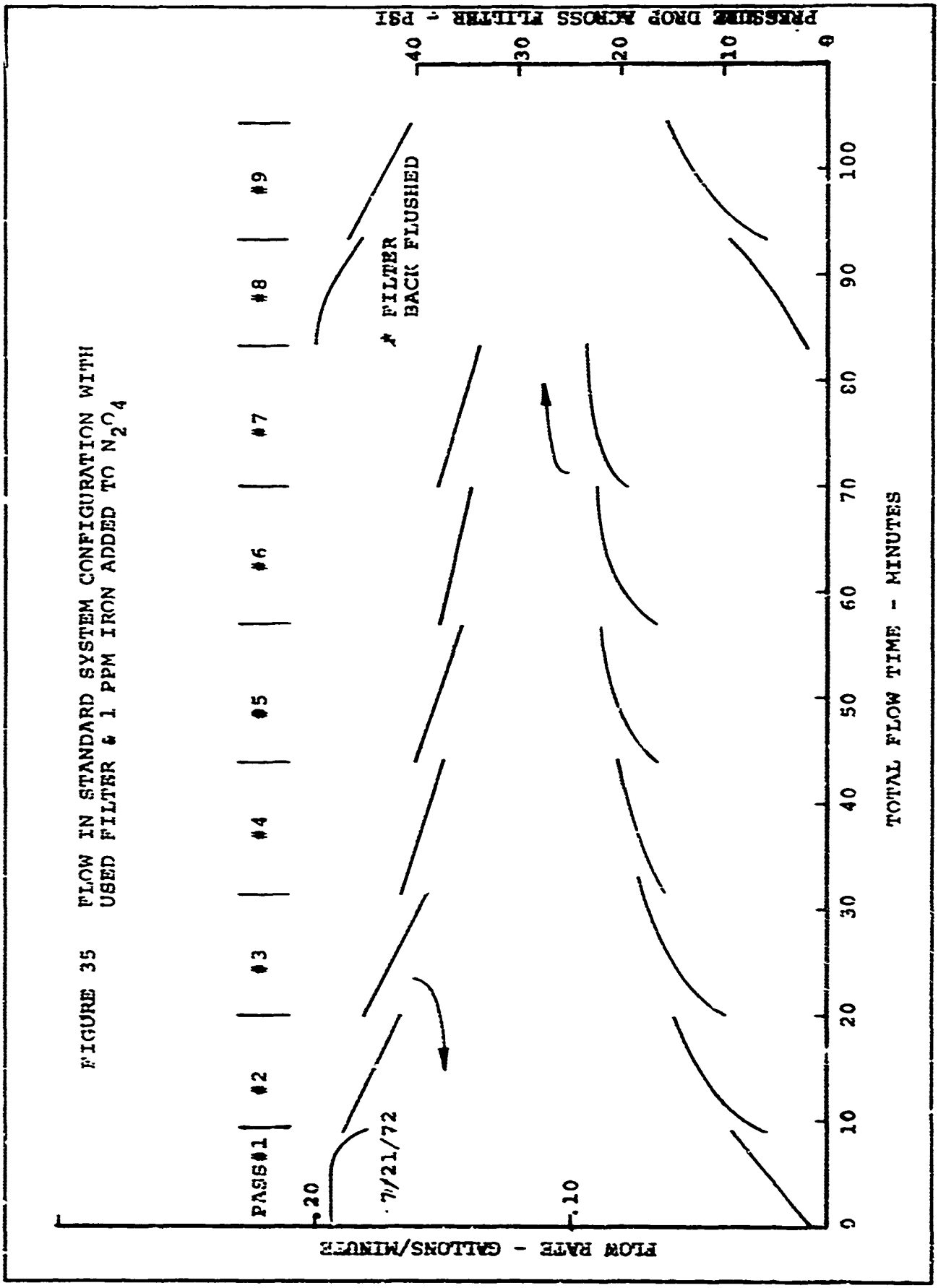


FIGURE 35 FLOW IN STANDARD SYSTEM CONFIGURATION WITH USED FILTER & 1 PPM IRON ADDED TO N_2O_4

back flushing. These results also suggest a high degree of purity for the N_2O_4 after passing through the molecular sieve.

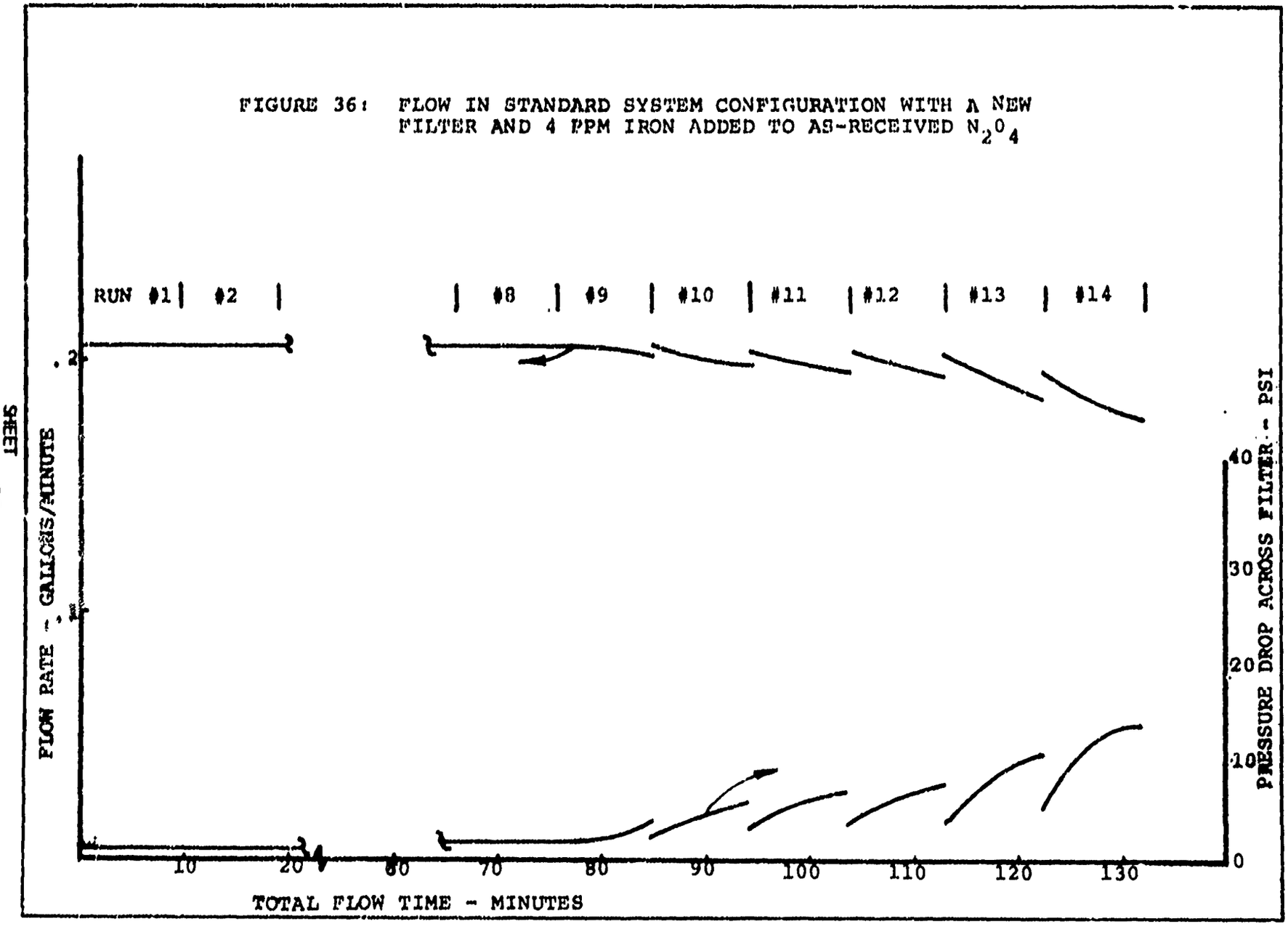
Another series of tests was run to determine the flow decay behavior in a system with different iron concentrations as before but with each using a new screen filter. The first test was run after the addition of 4 ppm of iron and, as indicated in Figure 36, decay occurred only after many (9) recirculations. The second test, with 3.6 ppm iron added, produced no decay even after 19 recirculations. In a third test with 10 ppm iron added the onset of flow decay occurred during recirculation #5 with greater intensity than for 4 ppm, Figure 37. From this data the added iron concentration for the onset of flow decay is concluded to be between 3.6 and 4.0 ppm for the flow system tested. Since the iron content of the as-received N_2O_4 was 0.5 ppm, this corresponds to a total iron concentration of 4.1 to 4.5 ppm.

6.3 FLOW OF DISTILLED N_2O_4 FOLLOWING STORAGE

Task 3 required that flow tests be performed with initially iron-free N_2O_4 after storage in tanks manufactured from 2014 aluminum, 6Al-4V titanium and 347 stainless steel. The tanks were thin-walled cylinders approximately 6" in diameter by 18" long (~2 gallon capacity) and were filled by distilling (to dryness) N_2O_4 from another 2 gallon aluminum tank. The filled tanks were allowed to sit at ambient temperature for 33 to 70 days before testing.

Prior to flow testing the test section was purged with gaseous nitrogen and the catch tank removed. Visual examination of the catch tank revealed apparently clean interior surfaces. However the tank was cleaned with a detergent wash, a water and a Freon rinse and was dried with hot nitrogen.

FIGURE 36: FLOW IN STANDARD SYSTEM CONFIGURATION WITH A NEW FILTER AND 4 PPM IRON ADDED TO AS-RECEIVED N_2O_4



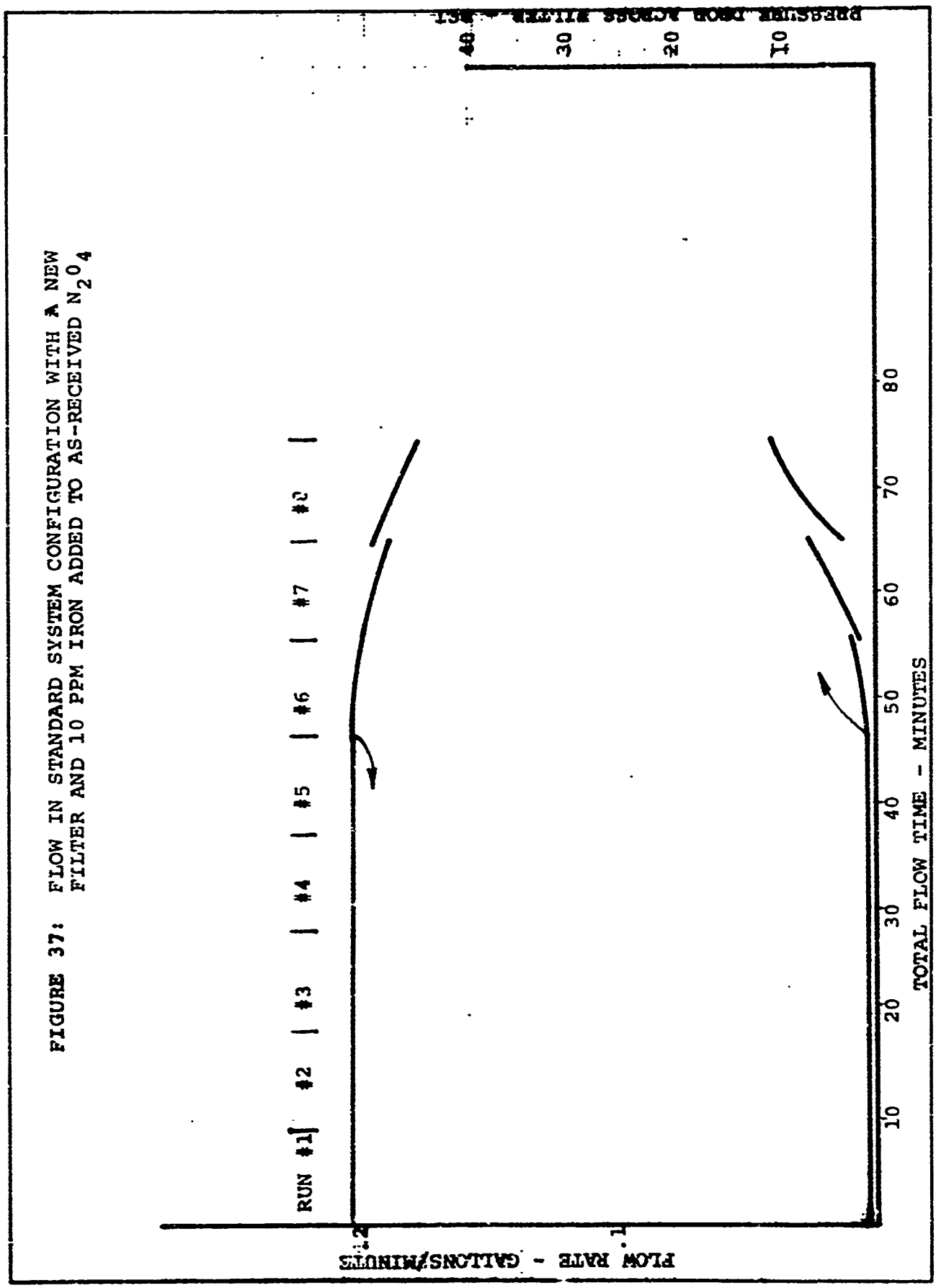


FIGURE 37: FLOW IN STANDARD SYSTEM CONFIGURATION WITH A NEW FILTER AND 10 PPM IRON ADDED TO AS-RECEIVED N_2O_4

The aluminum, titanium and stainless steel tanks were tested with new screen filters in that order, the expectation being that none of them would produce flow decay. The results, illustrated in Figures 38 and 39 evidence no flow decay for the 2014 aluminum or 347 stainless steel tanks. However, the 6Al-4V titanium tank produced a decay of about 15%, Figure 40.

In order to check the anomalous titanium data the filter which had become partially clogged was analyzed for titanium. This was accomplished by rinsing the filter with 5 ml of an aqueous solution containing 33% HNO_3 and 2% HF. The solution was then found by atomic absorption to contain 12 ppm titanium. From earlier experiments[7] with gre N_2O_4 which indicate that 1-10% of the clogging material acc es on the filter a possible concentration of .67 ppm of ti ium is indicated in the N_2O_4 in the titanium tank.

Other workers have studied the compatibility of N_2O_4 with 6Al-4V titanium. Reference 9 concludes that after a 28 day corrosion study a gelatinous precipitate was observed that "could affect the functioning of filters and valves in propulsion systems."

To further confirm the presence of possible metallic clogging complexes a sample of the N_2O_4 from the titanium tanks was analyzed for titanium and for iron. A 100 cc sample was withdrawn and concentrated by a factor of 20 for atomic absorption analysis. The detection sensitivity of the spectrometer was 10 ppm for titanium and $\sim$.03 ppm for iron. In the analysis titanium was not found but iron was present at a level of 10 ppm in the 5 cc water test solution. This corresponds to an iron concentration in the N_2O_4 of .35 ppm. The atomic absorption detection sensitivity for titanium inferred that the titanium concentration in the N_2O_4 was less than .35 ppm.

FIGURE 38: FLOW IN STANDARD SYSTEM CONFIGURATION WITH DISTILLED N_2O_4 AFTER 63 DAY STORAGE IN 2014 ALUMINUM TANK

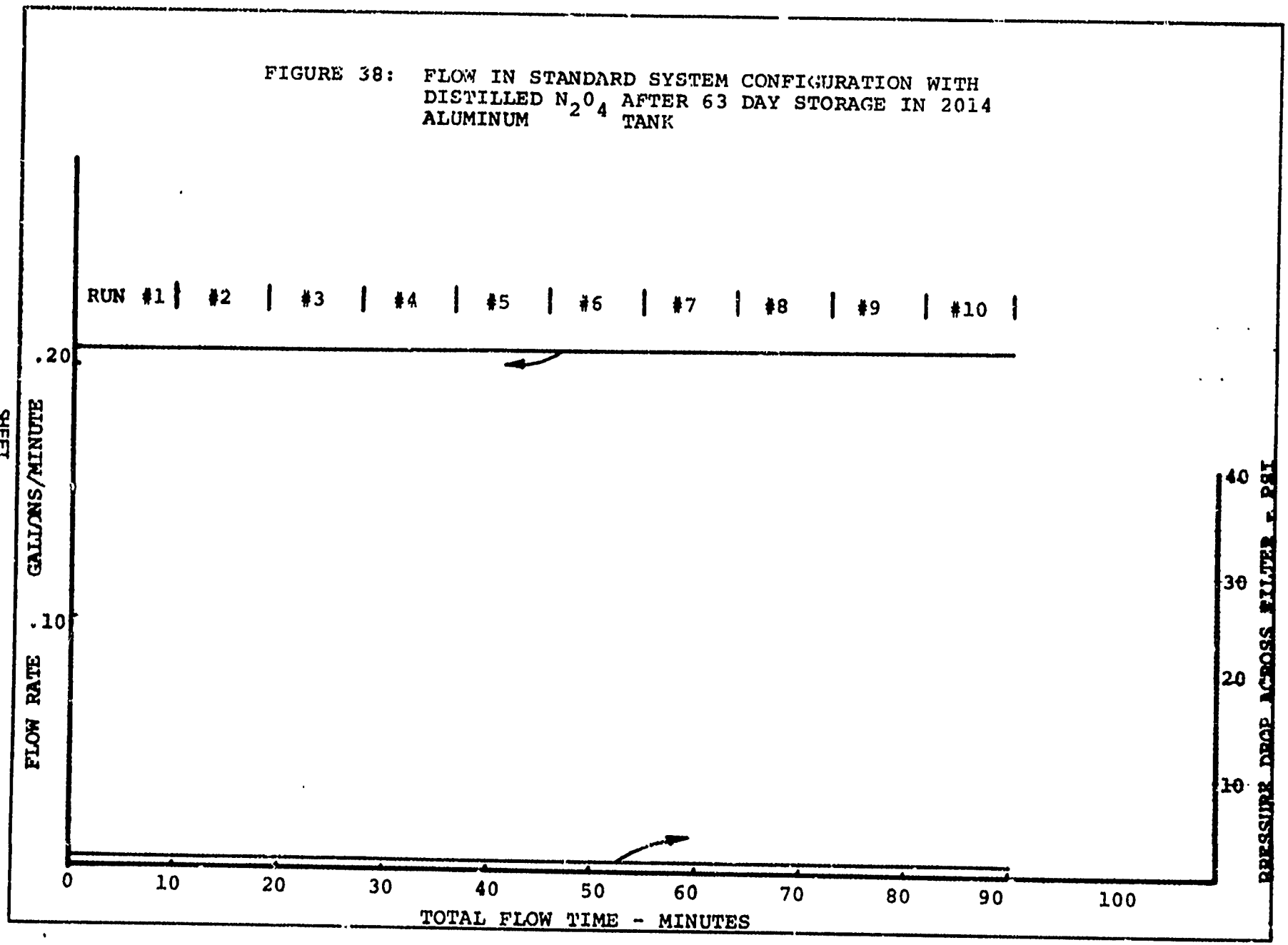
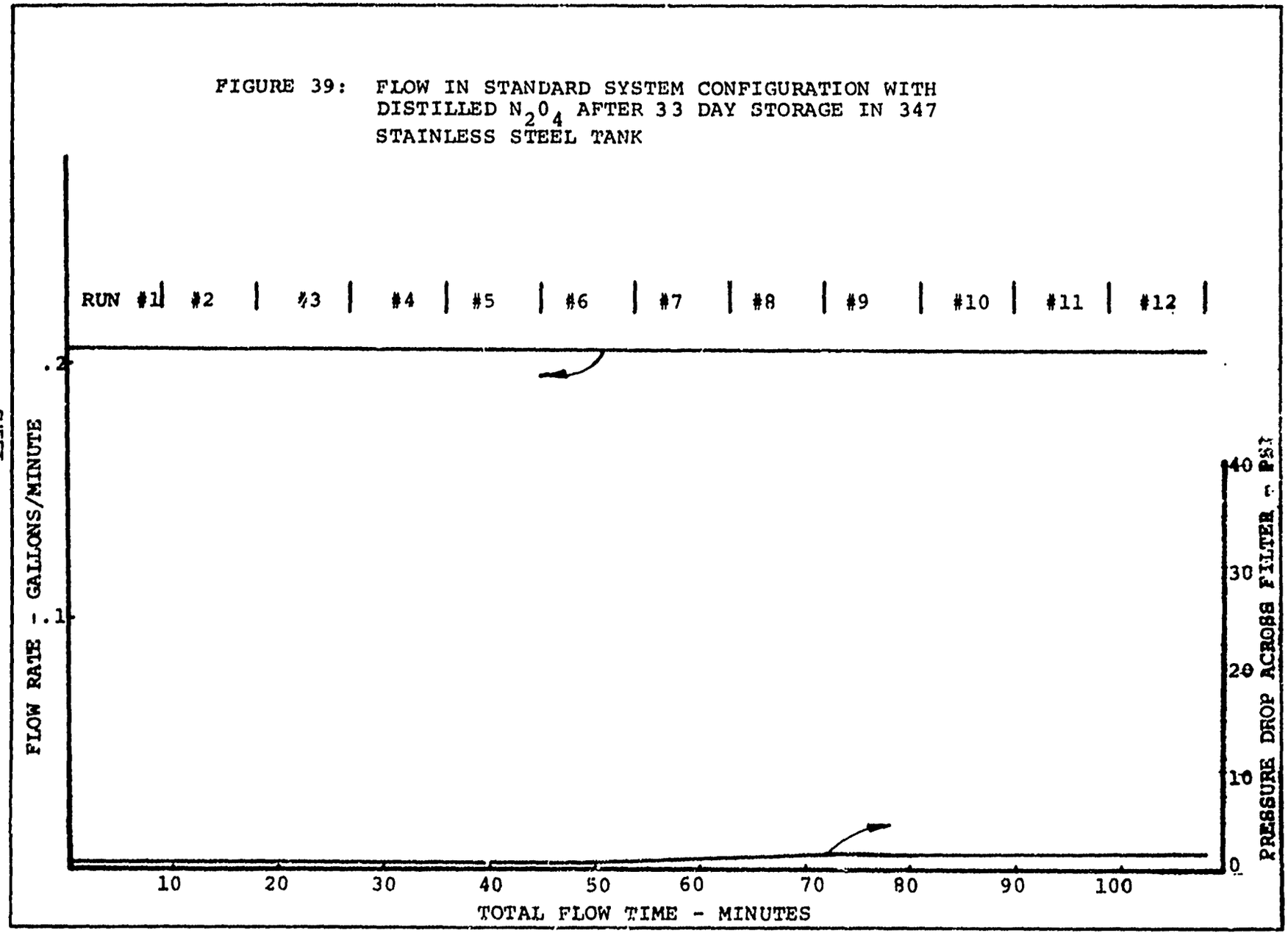


FIGURE 39: FLOW IN STANDARD SYSTEM CONFIGURATION WITH DISTILLED N_2O_4 AFTER 33 DAY STORAGE IN 347 STAINLESS STEEL TANK



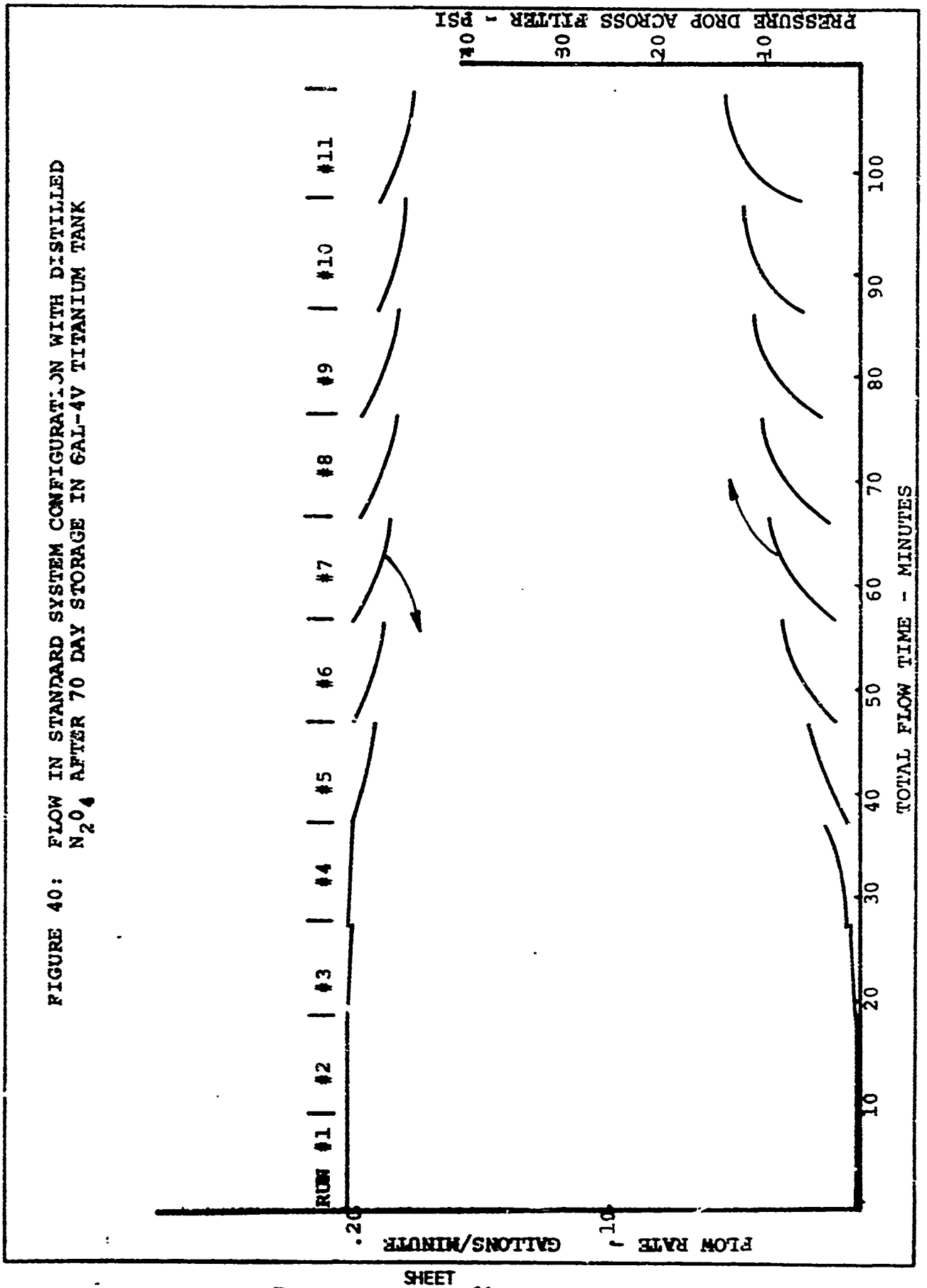


FIGURE 40: FLOW IN STANDARD SYSTEM CONFIGURATION WITH DISTILLED N_2O_4 AFTER 70 DAY STORAGE IN 6AL-4V TITANIUM TANK

The preceding results support the idea that the titanium tank reacted with the N_2O_4 (as evidenced by both the previous radioactive counting experiments and the analysis of washings from the filter). A past study[9] has shown that there is a stress-induced corrosion reaction between brown N_2O_4 and 6Al-4V titanium. Since the tanks used in these experiments were rolled to a 3" radius (thus leaving them in a somewhat stressed condition) some corrosion might be expected. However, the iron presents an enigma. There appears to be no reasonable way for it to enter the system except by reaction with the 8" length of stainless steel tubing in the test section or with the stainless steel filter itself. Yet, the small contact area and contact time are not consistent with an iron concentration of this magnitude.

One other possible way for this amount of iron to be present would be for iron to accumulate in the test section during previous runs, since it was not dismantled and cleaned prior to these particular tests. However, this possibility seems remote since radio tracer experiments had shown a uniform distribution of iron nitrate when added to a long tube of N_2O_4. Settling was not observed to occur. In addition the N_2O_4 from the titanium tank was flowed in between that from the aluminum and stainless steel tanks in which no decay occurred.

At this point no firm statement can be made relative to the cause of the flow decay experienced with the N_2O_4 from the titanium tank. It appears that the N_2O_4 did react with the tank but the effect this has on flow decay is unestablished.

6.4 Final Flow Testing

Questions as to whether the nature of the iron nitrate solution used to dope the as-received N_2O_4 would affect the flow decay precipitated two final tests. A fresh batch of iron nitrate

was prepared by dissolving iron wire in twice as much nitric acid as had previously been used. This meant that iron was added to the N_2O_4 at a rate of .5 ppm per .1 cc of nitrate solution rather than 1 ppm per .1 cc. Tests were run using clean filters with tanks of as-received N_2O_4 containing 5 ppm or 17.5 ppm iron from this freshly prepared solution.

No flow decay was observed during 10 recirculations of the N_2O_4 with 5 ppm iron or in 5 recirculations of that containing 17.5 ppm. Decay was expected in both cases. After sitting over the week end the latter fluid was again flowed 7 times with no clogging. The tank was allowed to sit for an additional two weeks and 4 recirculations were made with no change in flow behavior. The tank was then agitated by vigorous shaking and another five runs made. Flow decay was immediately experienced although it stabilized at a final flow of 90% of full scale.

At the conclusion of the flow testing, the N_2O_4 was poured from the tanks which were purged with dry nitrogen, flushed with Freon and dried with hot nitrogen. The tank interiors were then examined visually by inserting a small light into the tank and observing the inside through hydraulic fitting holes. In the tank containing 5 ppm a single reddish brown spot was observed on the bottom of the tank, having an approximate area of 1/16 sq. in. and an estimated thickness of 1/16". In the tank containing 17.5 ppm iron the interior surface appeared dull as a consequence of material adhering to the surface. Both of these observations are in contrast to the clean condition of the tank surface following extended use of the first batch of iron nitrate. These results emphasize the need for examination of the influence of other factors in addition to iron concentration in the flow decay process.

6.5 Discussion

One of the most significant results of the brown N_2O_4 flow tests was that the iron concentration threshold below which no flow decay occurred was an unusually high 4.1 ppm. Previous studies by other workers had shown flow decay at lower concentrations. In fact, in Boeing's own previous work in 1970 with green N_2O_4, flow decay was observed at iron concentrations as low as 0.3 ppm, and the degree of flow decay was proportional to the iron concentration added, with almost complete clogging occurring at 1 ppm.[7]

Although the previous flow system was constructed of stainless steel and the present of aluminum, both series of tests were otherwise quite similar. The question then arises as to whether there is a basic difference between the MSC-PPD-2A ("green" N_2O_4) and MIL-P-26539C ("brown" N_2O_4) applications. One should be wary of such generalizations, bearing in mind that concentrations of impurities such as H_2O and NOCl may be more important than the NO concentration (which causes the green color) in determining flow decay behavior. There would appear, however, to be a basic difference in the two types of N_2O_4 used in the two Boeing studies. Not only were the iron concentration thresholds different, but also the behavior of the iron upon addition to the N_2O_4. In both studies iron was added to distilled N_2O_4 in the form of ferric nitrate dissolved in a small amount of concentrated HNO_3. However, in the 1970 study radioactive tracers showed that the iron rapidly settled to the bottom of the tank, while in the present study a uniform solution with no indication of settling resulted. The question of whether an "equilibration" period would have an effect is unanswered. Prior to some of the flow tests in this study the N_2O_4 containing the added iron was allowed to sit many days with occasional shaking prior to commencing flow. Such an equilibration period had no apparent effect on increasing the tendency for flow decay to occur.

7.0 CONCLUSIONS

As a result of this study, four principal conclusions can be drawn:

1. Distillation, or filtration through Linde type 13X molecular sieves will remove filter clogging iron components from brown N_2O_4.
2. Molecular sieve filters appear adaptable to operational or field use to purify N_2O_4.
3. The order of preference for the storage tank materials tested is 2014 aluminum, 347 stainless steel and 6Al-4V titanium.
4. Uncertainties exist as to the influence of factors other than iron concentration on the occurrence of flow decay.

Subject to the constraints of conclusion number 4, the generalization may be made that flow decay can be prevented by removal of the iron nitrate complexes prior to loading a storage tank with N_2O_4. The resulting rate of iron build-up will influence how long the system may be safely stored. Although data from the 347 stainless steel/N_2O_4 system (Section 5.2) indicate an encouragingly slow rate of iron build-up for surface-to-volume ratios of interest, one should not conclude that other ferrous alloys will necessarily behave similarly.

While it was beyond the scope of the present effort to study the role of factors other than iron concentration in affecting flow decay, parameters such as temperature, flow rate, filter type, and impurity concentration (e.g., NO, NOCl, H_2O, dissolved metals other than iron), may be very important to the f w decay process. Knowledge of the role of these factors would undoubtedly clarify some of the data recorded in this study.

8.0 RECOMMENDATIONS

Following the demonstration of an efficient filter for purifying

brown N_2O_4, attention should now be directed to elucidating the filter design. Parameters such as filter particle size, flow rate, pressure drop, and filter length-to-diameter ratio should be related to filter efficiency. Filter design should be optimized from the standpoint of operational requirements such as filter shelf life, storage conditions, operational readiness, frequency of use and total filtration capacity.

Conditions affecting the entry of iron nitrate into solution with N_2O_4 need further definition. For example the effect on the rate of iron buildup of the concentration of H_2O, NO and NOCl in N_2O_4 should be investigated. In addition the effect of concentration of these compounds on flow decay behavior for a fixed iron concentration needs definition. Finally, the changes in flow caused by adding other metal complexes, such as titanium compounds, to the iron, H_2O, NO, and NOCl combinations should be analyzed.

The elucidation of an optimum filter design and the further definition of other flow decay parameters can best be established by a matrix of tests that would identify the interdependence of the different variables.

9.0 REFERENCES

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5. Ibid Title, TRW Interim Report 08113-6016-R000, October 1968.

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8. "A Study of the Mechanism of Chemical Reactivity of Nitrogen Tetroxide with Titanium Alloy," Hercules Research Center Report, HRC-68-2, August 1968.

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APPENDIX A

FLOW DECAY PREVENTION HANDBOOK PROCEDURE

Introduction

A major consequence of the contract F04611-72-C-0040 issued by the Air Force Rocket Propulsion Laboratory entitled "A Method for the Prevention of N_2O_4 Flow Decay" was the demonstration that molecular sieves could be used to prevent flow decay. Subsequent to filtration of brown N_2O_4 through Linde type 13X sieves, flow decay did not occur. Thus, in situations where flow decay is an actual or anticipated problem, the established procedures for handling N_2O_4 would benefit by changes to permit the incorporation of such a filter.

Since the introduction of a new component into a flow system is procedurally trivial, only the construction and preparation of the component for service requires explanation. For the sake of illustration the use of the operational - type filter developed under the contract will be detailed. When the filtering column is loaded with 0.2 lb of the molecular sieves described below, a flow rate of about 0.7 lb/min can be achieved when the supply tank is pressurized at 40 psig. The weight of the N_2O_4 passed through the column should be no more than 1000 times the weight of the sieves. This kind of filter is suitable for use with moderate amounts of N_2O_4 (no more than 200 lb). Where massive quantities of N_2O_4 are to be filtered, a larger size would be required but no problems relating to scalability are anticipated.

Filter Construction and Preparation

1. Procure the following components:

   1 - 30" length of 3/4" 5052 aluminum tubing

3 - 3/4" aluminum flare nuts
2 - 3/4" aluminum sleeves
1 - 3/4" 90° elbow, 5052 aluminum
1 - 2 micron filter, Western Filter Company, part number S12-19310-2
1 - 3/4" 5052 aluminum flared end cap
1 - 8 oz. can of Linde, 100/120 mish (Tyler standard) chromatographic grade, type 13X molecular sieves, Coast Engineering Laboratory, 13508 South Normandie Ave., Gardena, California 90249
1 - 3/4" 5052 flared end plug
1 - small package of glass wool

2. Install flare nuts and sleeves on 30" length of 3/4" tubing and flare both ends.
3. Clean all aluminum parts by agitating parts for 10 minutes in hot detergent solution (Ivory), rinse for 10 minutes in demineralized water, rinse for 15 minutes in a 50/50 solution of conc. nitric acid and water, rinse for 10 minutes with demineralizer water, rinse with acetone and dry.
4. Assemble the parts of the filter in the manner indicated in Figure B - 1. This the lower end of the filter.
5. Flush the tube with dry nitrogen for 2 minutes.
6. Open the can of sieves and quickly pour powder into the upper end of the filter tube. Transfer rapidly to avoid contamination with atmospheric moisture. Tap the tube lightly during filling to settle the sieve powder. Fill to within 1/4" of the lip of the flare.
7. Insert a small ball of glass wool into the top of the tube.
8. Install and tighten the end plug on top of the tube as shown in Figure B - 2.
9. When required for use remove the end plugs and insert filter into flow system.

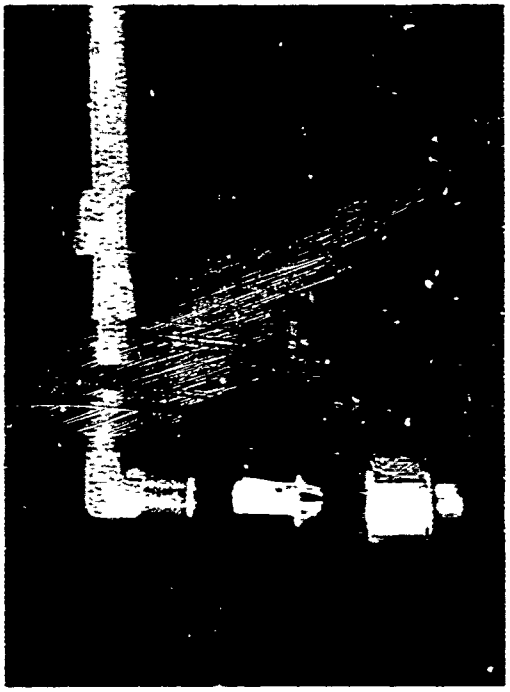

FIGURE A–1. EXPLODED VIEW OF LOWER END OF FILTER

FIGURE A–2. EXPLODED VIEW OF UPPER END OF FILTER